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# Rigid-Strut-Containing Crown Ethers and [2]Catenanes for Incorporation into Metal–Organic Frameworks

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**Abstract:** To introduce crown ethers into the struts of metal–organic frameworks (MOFs), general approaches have been developed for the syntheses of dicarboxylic acid dibenzo[30]crown-10 (DB30C10DA), dicarboxylic acid di-2,3-naphtho[30]crown-10 (DN30C10DA), dicarboxylic acid bis-paraphenylene[34]crown-10 (BPP34C10DA), and dicarboxylic acid 1,5-naphthoparaphenylene[36]crown-10 (NPP36C10DA). These novel crown ethers not only retain the characteristics of their parent crown ethers since they can 1) bind cationic guests and 2) serve as templates for making mechanically interlocked molecules (MIMs), such as catenanes and rotaxanes, but they also present coordination sites to connect with secondary building units (SBUs) in MOFs. The binding behavior of BPP34C10DA with 1,1′-dimethyl-4,4′-bipyridinium bis(hexafluorophosphate) (DMBP·2 $PF_6$) has been investigated by means of UV/Vis, fluorescence, and NMR spectroscopic techniques. The crystal superstructure of the complex DMBP·2 $PF_6$⊂BPP34C10DA was determined by X-ray crystallography. The NPP36C10DA-based [2]catenane ($H_2$NPP36C10DC-CAT·4 $PF_6$) and the BPP34C10DA-based [2]catenane ($H_2$BPP34C10DC-CAT·4 $PF_6$) were prepared in DMF at room temperature by the template-directed clipping reactions of the planarly chiral NPP36C10DA and BPP34C10DA with 1,1′-[1,4-phenylenebis(methylene)]di-4,4′-bipyridin-1-ium bis(hexafluorophosphate) and 1,4-bis(bromomethyl)-benzene, respectively. The crystal structure of the dimethyl ester (BPP34C10DE-CAT·4 $PF_6$) of the [2]catenane $H_2$BPP34C10DC-CAT·4 $PF_6$ was investigated by X-ray crystallography, which revealed racemic *R* and *S* isomers with planar chirality present in the crystal in a 1:1 ratio. These crown ether based struts serve as excellent organic ligands to bind with transition metal ions in the construction of MOFs: the crown ethers BPP34C10DA and NPP36C10DA in the presence of $Zn(NO_3)_2$·4 $H_2O$ afforded the MOF-1001 and MOF-1002 frameworks, respectively. The crystal structures of MOF-1001 and MOF-1002 are both cubic and display $Fm\bar{3}m$ symmetry. The unit cell parameter of the metal–organic frameworks is $a$ = 52.9345 Å. Since such MOFs, containing electron-donating crown ethers are capable of docking incoming electron-accepting substrates in a stereoelectronically controlled fashion, the present work opens a new access to the preparation and application of MOFs.

**Keywords:** catenanes · crown ethers · macrocyclic ligands · metal–organic frameworks · solid-state structures

## Introduction

Since the so-called crown ethers were discovered by Pedersen in 1967,[1] they have led to a wide variety of applications in supramolecular chemistry, materials science, nanoscience, and so on.[2] One of the most significant properties for crown ethers is that they can serve as hosts for binding inorganic and organic guests, especially cationic ones.[1a] On account of this important property, particular crown ethers have been employed as templates in the construction of mechanically interlocked molecules (MIMs), such as catenanes and rotaxanes.[3,4] To expand the collection of functional materials that can be applied to address some of the technolog-

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ical needs of today's society, such as those of stimuli-responsive materials, drug delivery systems, gas-storage materials, or sensors for environmental monitoring, medical diagnostics, and gene-chip technologies, the preparation of novel crown ethers have been highly sought after in recent years. The relatively difficult preparation and modification of crown ethers, however, limit their applications. Thus, it is currently desirable to develop general synthetic approaches for the preparation and modification of functioning crown ethers.

Crown ethers are flexible compounds,[2a] a situation that may result in many possible conformations when they express their binding properties. To decrease conformational space, aromatic residues have been introduced into their constitutions to impart increased rigidity.[5] Since the [*n*]crown-10 analogues, namely, bisparaphenylene[34]crown-10 (BPP34C10),[6] 1,5-naphthoparaphenylene-[36]crown-10 (NPP36C10),[7] dibenzo[30]crown-10 (DB30C10),[8] and di-2,3-naphtho[30]-crown-10 (DN30C10),[8] are good macrocyclic polyethers for the construction of MIMs by templation, we herein describe the general syntheses of relatively rigid aromatic crown ethers, namely, dicarboxylic acid DB30C10 (DB30C10DA), dicarboxylic acid DN30C10 (DN30C10DA), dicarboxylic acid NPP36C10 (NPP36C10DA), and dicarboxylic acid BPP34C10 (BPP34C10DA), and the preparation and characterization of the NPP36C10DA-based [2]catenane ($H_2$NPP36C10DC-CAT•4$PF_6$), the BPP34C10DA-based [2]catenane ($H_2$BPP34C10DC-CAT•4$PF_6$), the dimethyl ester (BPP34C10DE-CAT•4$PF_6$) of the [2]catenane $H_2$BPP34C10DC-CAT•4$PF_6$, and the complex (DMBP•2$PF_6$⊂BPP34C10DA) of BPP34C10DA with 1,1′-dimethyl-4,4′-bipyridinium bis(hexafluorophosphate) (DMBP•2$PF_6$). Sonogashira couplings[9] are general approaches developed in this research toward the synthesis of the dicarboxylic acid terminated rigid struts. To establish the best synthetic approaches for the preparation of these crown ethers, successful and unsuccessful synthetic approaches carried out by us are described and discussed. Crown ethers and [2]catenanes carrying two carboxylic acid units can serve as organic ligands to coordinate with secondary building units (SBUs) for the preparations of metal–organic frameworks (MOFs).[10] The crown ethers BPP34C10DA and NPP36C10DA in the presence of $Zn(NO_3)_2$•4$H_2O$ have afforded[11] MOF-1001 and MOF-1002 frameworks, respectively. The crystal structures of MOF-1001 and MOF-1002 provide direct evidence for the formation of extended frameworks. The advantages of these crown ethers in the preparations of MOFs are that 1) the crown ethers with an approximately 2 nm strut length—the distance between the two carbon atoms of the terminal carboxyl groups—are expected to be employed in the synthesis of MOFs with extra large pores, 2) the uncomplexed crown ethers in the MOFs can bind certain guest molecules, and 3) this synthetic strategy may lead to new properties for MOFs, for example, chirality, provided that the appropriate crown ether derivatives can be resolved.

**Abstract in Chinese:**

为了使用冠醚构筑金属-有机构架(MOFs)材料，我们发展了一类合成方法制备含有二羧酸基团的冠醚，即，二苯并[30]冠-10 二羧酸(DB30C10DA)、2,3-二萘并[30]冠-10 二羧酸(DN30C10DA)、二对苯并[34]冠-10 二羧酸(BPP34C10DA)以及 1,5-萘并对苯并[36]冠-10 二羧酸(NPP36C10DA)。研究发现，这类新型的冠醚不但继续保持着冠状化合物的特性：(i)它们能够键合阳离子客体，(ii)它们能够作为模板制备索烃和轮烷等机械互锁分子(MIMs)，而且还能够与金属簇配位形成 MOF 材料。紫外光谱、荧光光谱和核磁实验研究结果显示冠醚 BPP34C10DA 和 1,1′-二甲基-4,4′-联吡啶六氟磷酸盐(DMBP•2$PF_6$)阳离子能够在溶液中形成包结配合物(DMBP•2$PF_6$⊂BPP34C10DA)，X 射线晶体分析也揭示出了该配合物在固相中的主-客体包结构象。运用模板导向的合成方法，我们进一步制备得到了基于冠醚 NPP36C10DA 和 BPP34C10DA 的[2]索烃 $H_2$NPP36C10DC-CAT•4$PF_6$ 和 $H_2$BPP34C10DC-CAT•4$PF_6$。[2]索烃 $H_2$BPP34C10DC-CAT•4$PF_6$ 的二甲酯衍生物(BPP34C10DE-CAT•4$PF_6$)也通过类似的方法合成。X 射线晶体分析显示消旋的(*R*)-和(*S*)-BPP34C10DE-CAT•4$PF_6$ 手性异构体以 1:1 的比例共存于晶胞中，证明了该类冠醚及其[2]索烃平面手性的存在。更有意义的是，冠醚 BPP34C10DA 和 NPP36C10DA 能够分别与 $Zn(NO_3)_2$•4$H_2O$ 配位形成金属-有机构架材料 MOF-1001 和 MOF-1002。MOF-1001 和 MOF-1002 的晶体结构属于立方晶系并且拥有 $Fm\bar{3}m$ 空间群，它们的晶胞参数是 $a$ = 52.9345 Å。由于该类 MOF 材料含有众多拥有给电子能力的冠醚，具有电子接受能力的客体分子能够被选择性地键合到 MOF 的冠状结构中，从而为 MOF 材料的制备和应用开辟了一个新的方向。

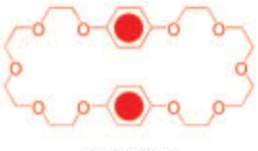
## Results and Discussion

**Synthesis**: In this section, we describe in detail the synthetic procedures employed in the preparation of the target crown ethers and [2]catenanes. An important starting material, methyl 4-ethynylbenzoate (**2**), was prepared by two approaches (see I and II in Scheme 1) from methyl 4-iodobenzoate and ethyl 4-bromobenzoate, respectively. In route I, compound **2** was prepared from **1** in a yield of 95% according to a similar procedure in literature.[12] In route II, ethyl 4-trimethylsilyl-ethynylbenzoate (**3**) was formed by reacting ethyl 4-bromobenzoate and (trimethylsilyl)acetylene in a yield of 94%. Compound **2** was obtained from **3** in MeOH with a yield of 99% by desilylation and transesterification from ethyl benzoate to methyl benzoate. Both these routes are efficient for the preparation of **2**.

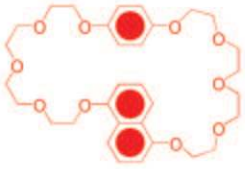
As the control compounds for the linearly rigid-strut-containing crown ethers, the struts **8** and **14** were prepared by using the approaches outlined in Schemes 2 and 3, respectively. 1,4-Diethynyl-2,5-dimethoxybenzene (**6**) and 1,4-diethynyl-2,3-bis(methoxymethoxy)naphthalene (**12**) were prepared from 1,4-diiodo-2,5-dimethoxybenzene (**4**) and 1,4-dibromo-2,3-bis(methoxymethoxy)naphthalene (**10**), respectively, through coupling reactions with (trimethylsilyl)acetylene and subsequent desilylation procedures. Precursors **6** and **12** were further treated with methyl 4-iodobenzoate to afford the strut-containing di(methyl benzoate)s **7** and **13**, and finally, the struts **8** and **14** were obtained by de-esterification of **7** and **13** in yields of 98 and 95%, respectively.

The crown ether DB30C10DA was synthesized by using two different approaches, as outlined in Schemes 4 and 5. In the approach outlined in Scheme 4, 1,4-bis(trimethylsilyl)-2,3-dimethoxybenzene (**16**) was prepared from 1,2-dimethoxybenzene (veratrol) in two steps. Compound **16** was treated with ICl in $CH_2Cl_2$ to afford 1,4-diiodo-2,3-dime-

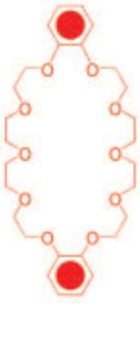
  



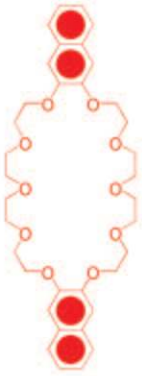
BPP34C10



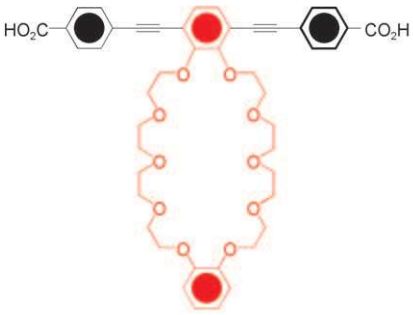
NPP36C10



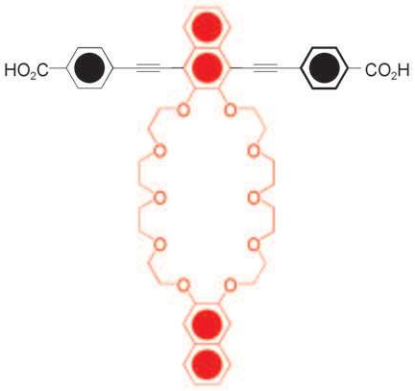
DB30C10



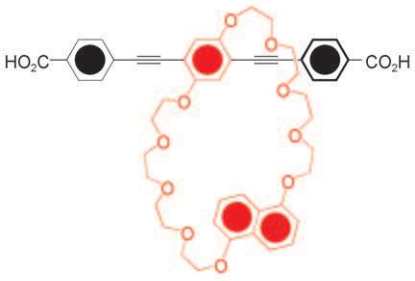
DN30C10



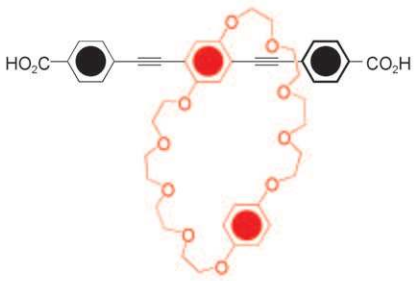
DB30C10DA



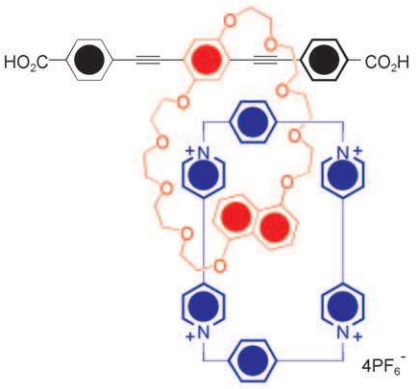
DN30C10DA



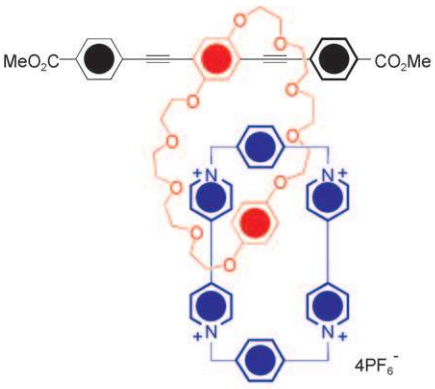
NPP36C10DA



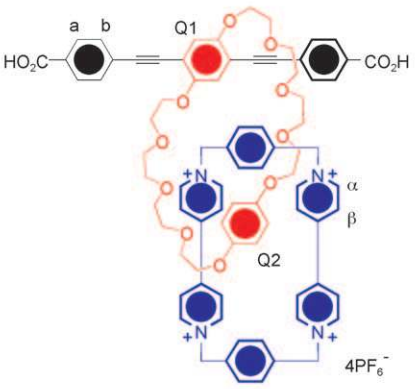
BPP34C10DA



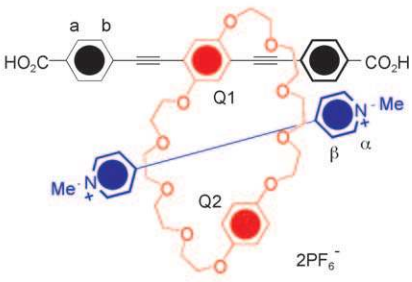
$H_2$NPP36C10DC-CAT•4$PF_6$



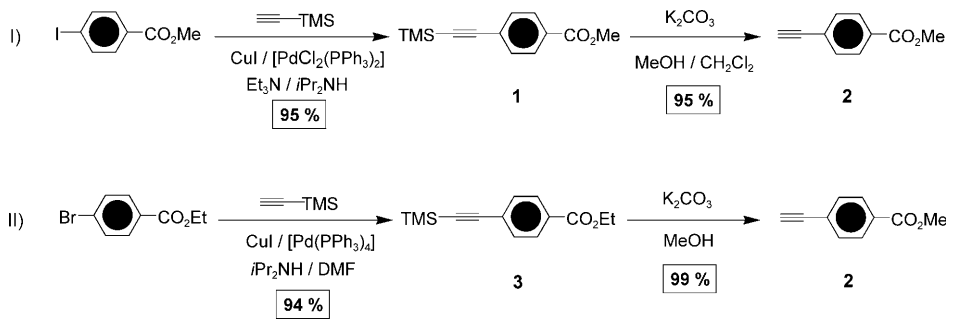
BPP34C10DE-CAT•4$PF_6$



$H_2$BPP34C10DC-CAT•4$PF_6$



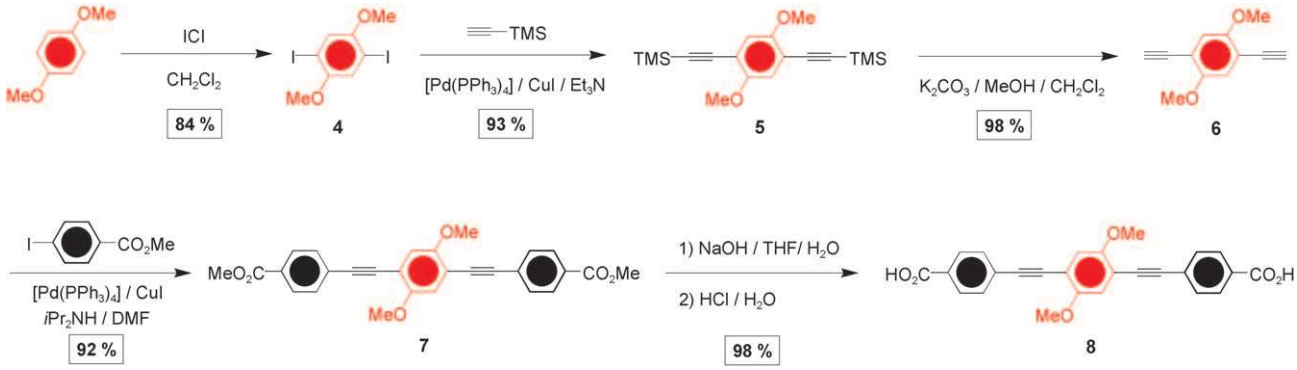
DMBP•2$PF_6$⊂BPP34C10DA



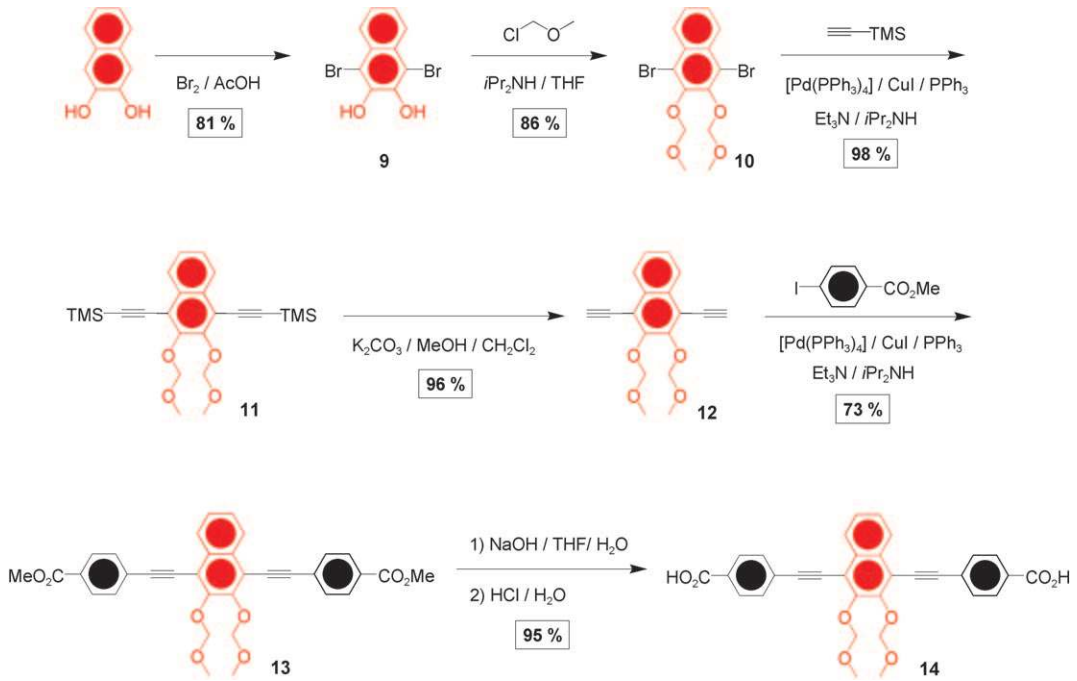

Scheme 1. The preparation of methyl 4-ethynylbenzoate (**2**). TMS = trimethylsilyl.

thoxybenzene (**17**). Since the two methyl groups in **17** are not good leaving groups, we replaced them by methoxymethyl groups to afford 1,4-diiodo-2,3-bis(methoxymethoxy)-benzene (**19**). The two methoxymethyl groups in the strut **20**, which was prepared by means of a coupling reaction of **19** with **2**, were removed to give the strut **21**. DB30C10DE was synthesized by the macrocyclization of the strut **21** with the ditosylate **23**. The crown ether DB30C10DA was then obtained by de-esterification and subsequent acidification of DB30C10DE in a total yield of 91%.

Since the yield of the macrocyclization for the preparation of DB30C10DE is relatively low (16%), we synthesized this crown ether by an improved approach (Scheme 5). In this

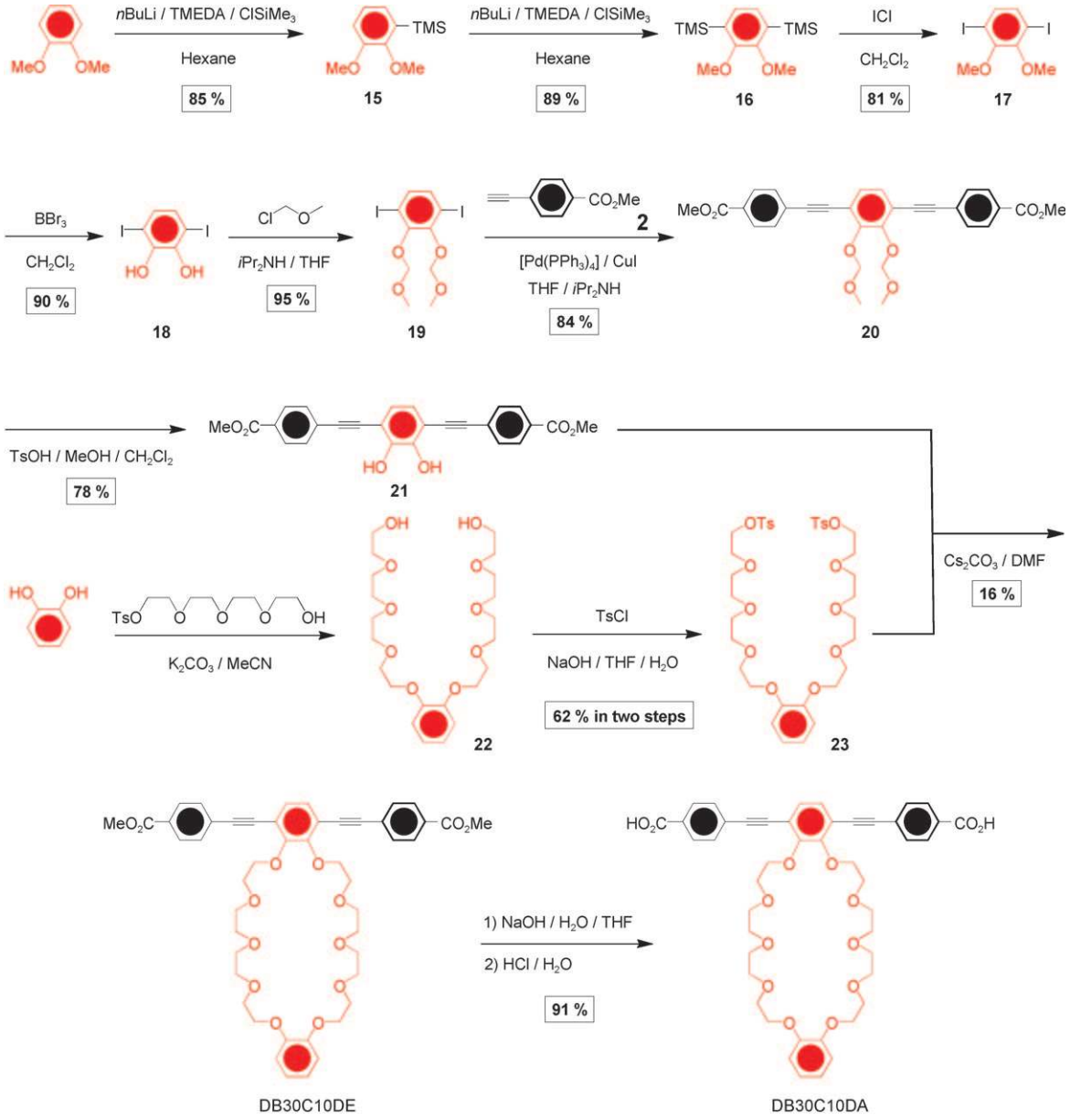



Scheme 2. The preparation of the strut **8**.




Scheme 3. The preparation of the strut **14**.



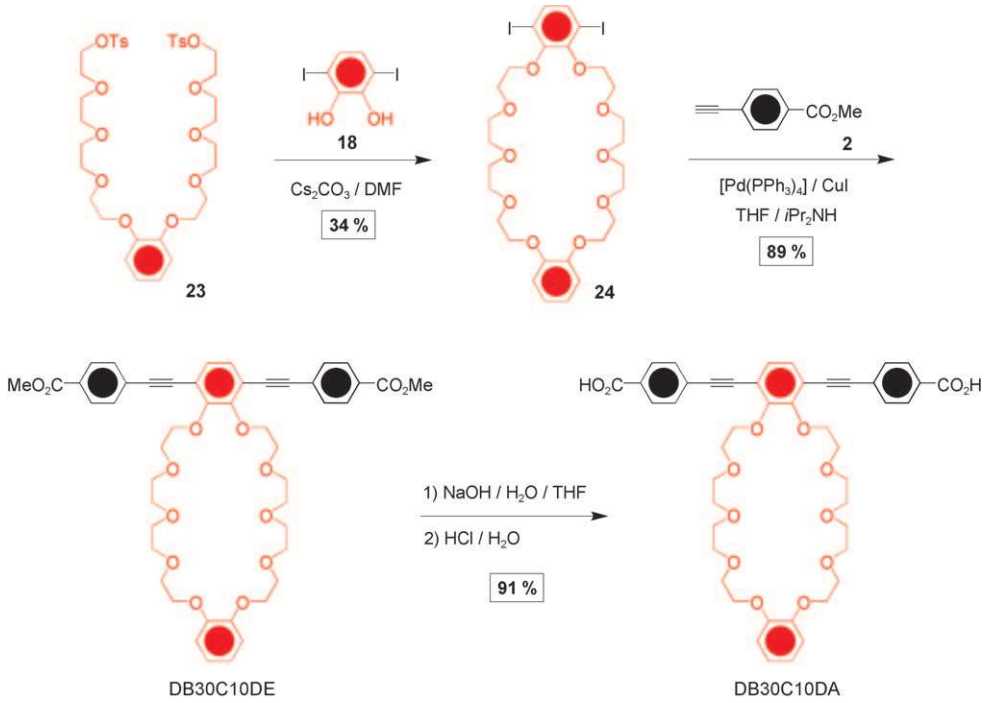

Scheme 4. The preparation of DB30C10DA. TMEDA = tetramethylethylenediamine.

approach, the precursor crown ether **24** was prepared through the macrocyclization of the ditosylate **23** with the diol **18** in a higher yield of 34%. After a coupling reaction between **24** and **2** was carried out, DB30C10DE can be isolated in a yield of 89%. Thus, the approach outlined in Scheme 5 is a preferable procedure for the preparation of DB30C10DA.

In analogy with the preparation of DB30C10DA, the crown ether DN30C10DA was also synthesized using the two approaches outlined in Schemes 6 and 7. In the approach outlined in Scheme 6, the crown ether DN30C10DE was synthesized by macrocyclization between the strut **25** and the ditosylate **27**. DN30C10DA can be obtained in a total yield of 84% by de-esterification and subsequent acidification of DN30C10DE. The approach outlined in Scheme 7 affords a better approach for the preparation of DN30C10DA. The precursor crown ether **28** was prepared through macrocyclization between the ditosylate **27** and the diol **9** in a higher yield of 39%. A coupling reaction between **28** and **2** was then carried out to give the crown ether DN30C10DE with a yield of 72%. DN30C10DA was finally prepared from DN30C10DE by using the same procedure as that described above.

The crown ether NPP36C10DA was synthesized by using the procedure shown in Scheme 8. The strut **30** carrying two tetraethyleneglycol chains on its central hydroquinone ring was prepared by a coupling reaction of **29** with **2**. The crown ether NPP36C10DE was then synthesized by the macrocyclization between the ditosylate **31** and 1,5-dihydroxynaphthalene in a yield of 20%. Thus, NPP36C10DA was obtained




Scheme 5. The preparation of DB30C10DA.

by de-esterification and subsequent acidification of NPP36C10DE in a total yield of 96%.

We employed five different approaches (Schemes 9–13), including some approaches similar to those employed in the syntheses of the crown ethers DB30C10DA, DN30C10DA, and NPP36C10DA, to prepare the crown ether BPP34C10DA. The approaches outlined in Schemes 9 and 10 for the preparation of BPP34C10DA are similar to that given in Schemes 5 and 7 used in the preparation of DB30C10DA and DN30C10DA, namely, macrocyclization between **33** and 2,5-dibromohydroquinone (or 2,5-diiodohydroquinone) was carried out to afford the precursor crown ether **34** (or **35**). After a coupling reaction between **34** (or **35**) and **2**, BPP34C10DE can be isolated. BPP34C10DA was obtained finally by de-esterification and subsequent acidification of BPP34C10DE in a yield of 94%. Overall, the approach outlined in Scheme 10 affords a more efficient route for the preparation of BPP34C10DA than that detailed in Scheme 9.

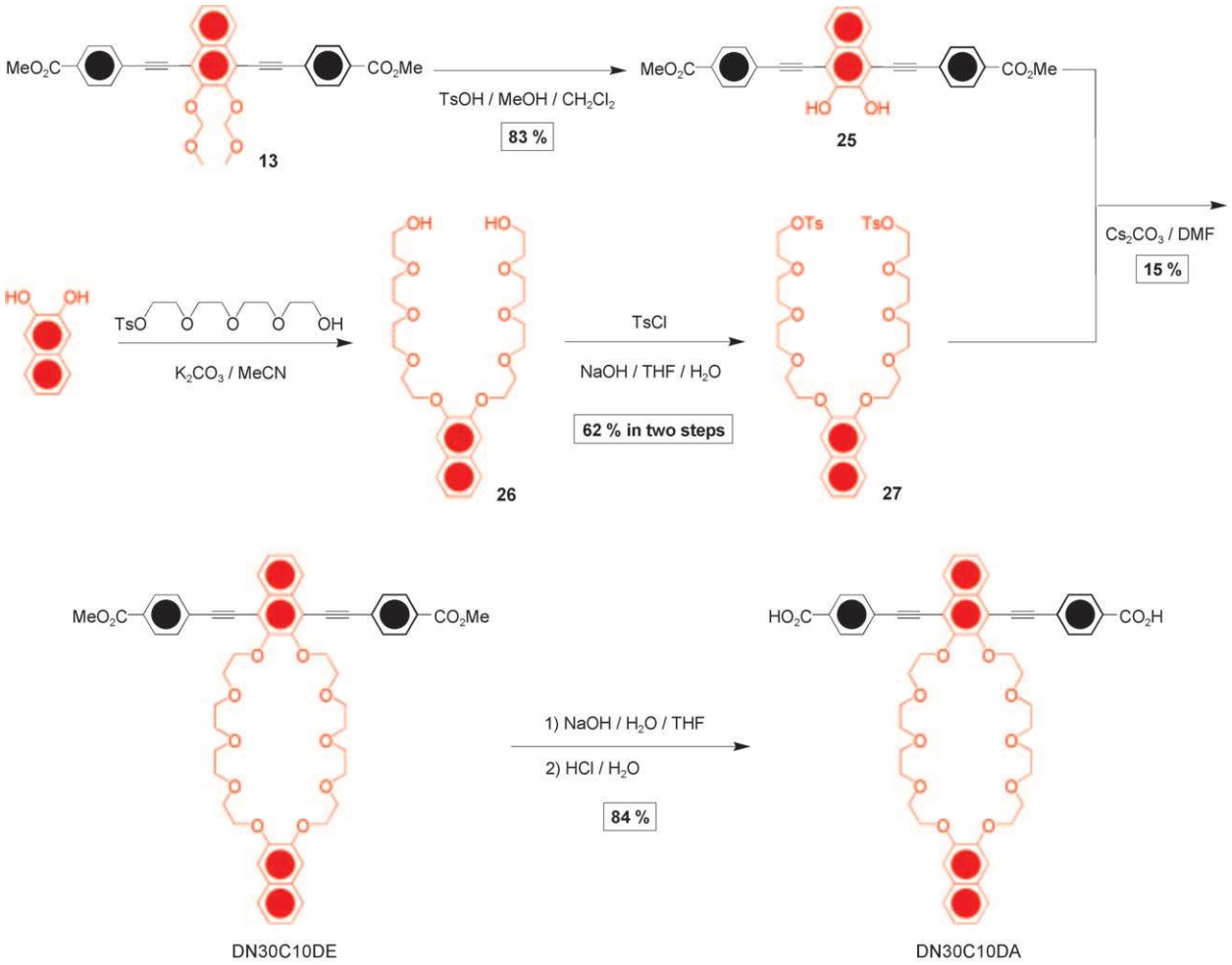
The procedure for the preparation of BPP34C10DA shown in Scheme 11 is similar to the one employed in the preparation of NPP36C10DA (Scheme 8). The crown ether BPP34C10DE was synthesized by the macrocyclization between the ditosylate **31** and hydroquinone in a yield of 24%. BPP34C10DA was then prepared from the crown ether BPP34C10DE according to the procedure described above.

Scheme 12 summarizes another procedure we have employed in the preparation of BPP34C10DA. The tetrahydropyranyl (THP)-protected 2,5-dibromohydroquinone **36** was transformed to the strut **39** in three steps with a series of coupling reactions. After the deprotection of the THP units in **39**, the resulting strut **40** was treated with the ditosylate **33** to give the crown ether BPP34C10DE in a relatively low yield of 10%. In a similar approach (Scheme 13), we carried out a deprotection to obtain the strut **40** from **7**. Since the strut **40** could not be isolated from its byproducts, the attempted preparation for the crown ether BPP34C10DA following the approach outlined in Scheme 13 failed. Thus, the approach detailed in Scheme 10 is the preferable procedure for the preparation of BPP34C10DA.

The [2]catenanes $H_2$NPP36C10DC-CAT·4$PF_6$, BPP34C10DE-CAT·4$PF_6$, and $H_2$BPP34C10DC-CAT·4$PF_6$ were prepared (Scheme 14) by the crown ethers NPP36C10DA, BPP34C10DE, and BPP34C10DA to template the formation of the mechanized interlocked cyclophanes from 1,1′-[1,4-phenylenebis(methylene)]di-4,4′-bipyridin-1-ium bis(hexafluorophosphate) and 1,4-bis(bromomethyl)benzene in DMF at room temperature. Following the reactions, the crude mixtures were purified by column chromatography on silica gel (MeOH/$NH_4Cl$ (2 M)/$MeNO_2$ = 7:2:1) to afford the corresponding [2]catenanes in yields of approximately 50%. The complex DMBP·2$PF_6$⊂BPP34C10DA was prepared from BPP34C10DA and DMBP·2$PF_6$ in a mixture of $Me_2CO$ and *n*-pentane at room temperature. When the solution was left at room temperature for three days, red block-shape crystals were obtained and were subjected to X-ray crystallographic analyses.

A promising application of the linear strut-containing crown ethers is the construction of MOFs. The crown ethers BPP34C10DA and NPP36C10DA coordinated by $Zn_4O$ clusters in $MeNH_2$/DMF at 65°C afforded MOF-1001 and



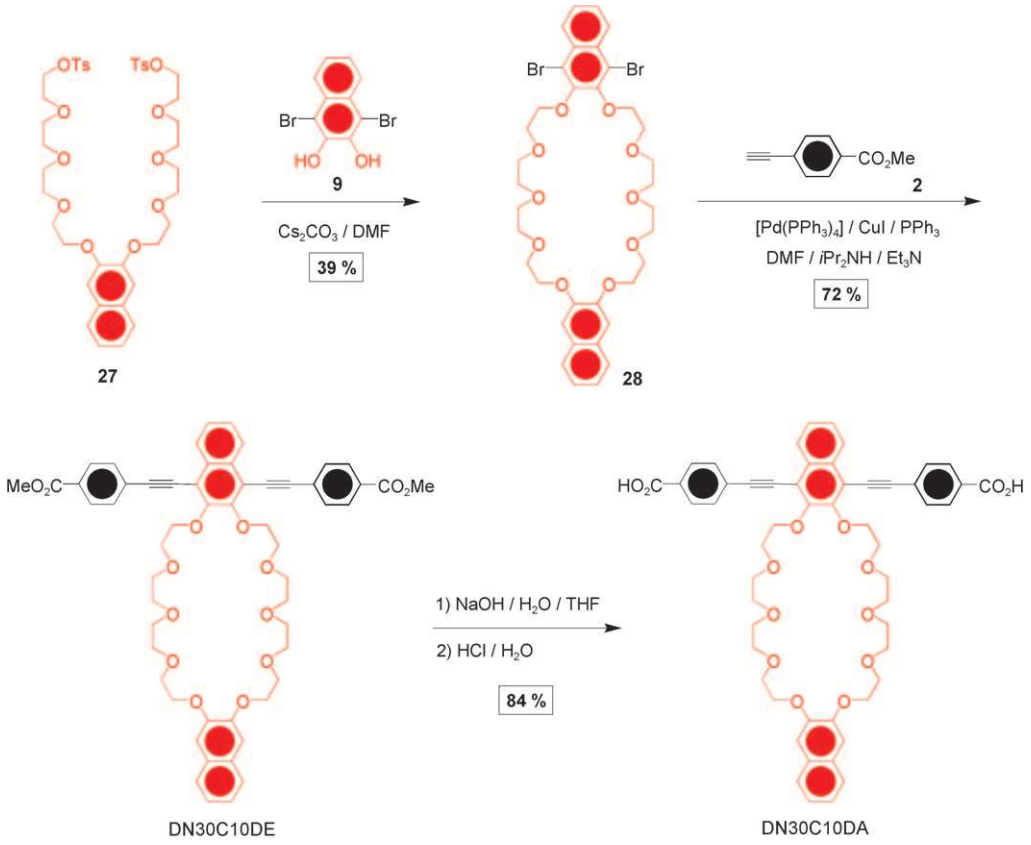

Scheme 6. The preparation of DN30C10DA.

MOF-1002, respectively. After the mixture solutions had cooled to room temperature slowly and naturally, light-yellow cubic crystals of MOF-1001 and MOF-1002 were collected for X-ray crystallographic analyses.

**UV/Vis, fluorescence, and NMR spectroscopies**: Since the crown ethers DB30C10DA, DN30C10DA, NPP36C10DA, and BPP34C10DA contain linearly conjugated struts, they showed significant fluorescent properties. It is well known that DMBP•2$PF_6$ and its derivatives are excellent dicationic guests for the 30-, 34-, and 36-membered crown ethers.[6,13] Thus, we employed BPP34C10DA and DMBP•2$PF_6$ as a model pair to investigate their binding behavior using UV/Vis and fluorescence spectrophotometers at room temperature. The $Me_2CO$ solution of BPP34C10DA turns to red after the addition of equimolar DMBP•2$PF_6$. In the UV/Vis spectra, BPP34C10DA shows (0.50 mM) a maximum absorption around 377 nm in $Me_2CO$ and the absorption band between 430–540 nm increases after the addition of the DMBP•2$PF_6$ guest. In the fluorescence spectra, the maximum fluorescence intensity ($\lambda = 458$ nm) of BPP34C10DA is quenched completely upon the addition of equimolar DMBP•2$PF_6$, the results indicate that the DMBP•2$PF_6$ guest is included inside the cavity of the BPP34C10DA macrocycle, leading to significant charge-transfer interactions between them. The binding constant ($K_a$) between BPP34C10DA and DMBP•2$PF_6$ in $Me_2CO$ was obtained by means of spectrophotometric titration. A value of ($829 \pm 71$) $M^{-1}$ was obtained.

The inclusion complexation formation of BPP34C10DA and DMBP•2$PF_6$ was evaluated further by means of $^1H$, $^{13}C$, $^{15}N$, $^1H$–$^1H$ COSY, and $^1H$–$^{13}C$ HMQC NMR spectroscopies. To improve the signal-to-noise ratio, isotope-enriched DMBP•2$PF_6$ with 25% abundance of $^{15}N$ was synthesized and employed in all of the NMR experiments. The protons in the complex were assigned fully by $^1H$–$^1H$ COSY and $^1H$–$^{13}C$ HMQC NMR experiments. In particular, the $^1H$–$^{13}C$ HMQC NMR spectrum (Figure 1) of DMBP•2$PF_6$ ($1.2 \times 10^{-3}$ M) and BPP34C10DA ($4.0 \times 10^{-4}$ M) shows the clear correlations between the protons and the related carbon nuclei in complexed and uncomplexed DMBP•2$PF_6$ (α, β, and methyl nuclei in the blue lines) and BPP34C10DA (a and b nuclei of the 4-carboxyphenylethynyl moieties in the black lines and Q1 and Q2 nuclei of the



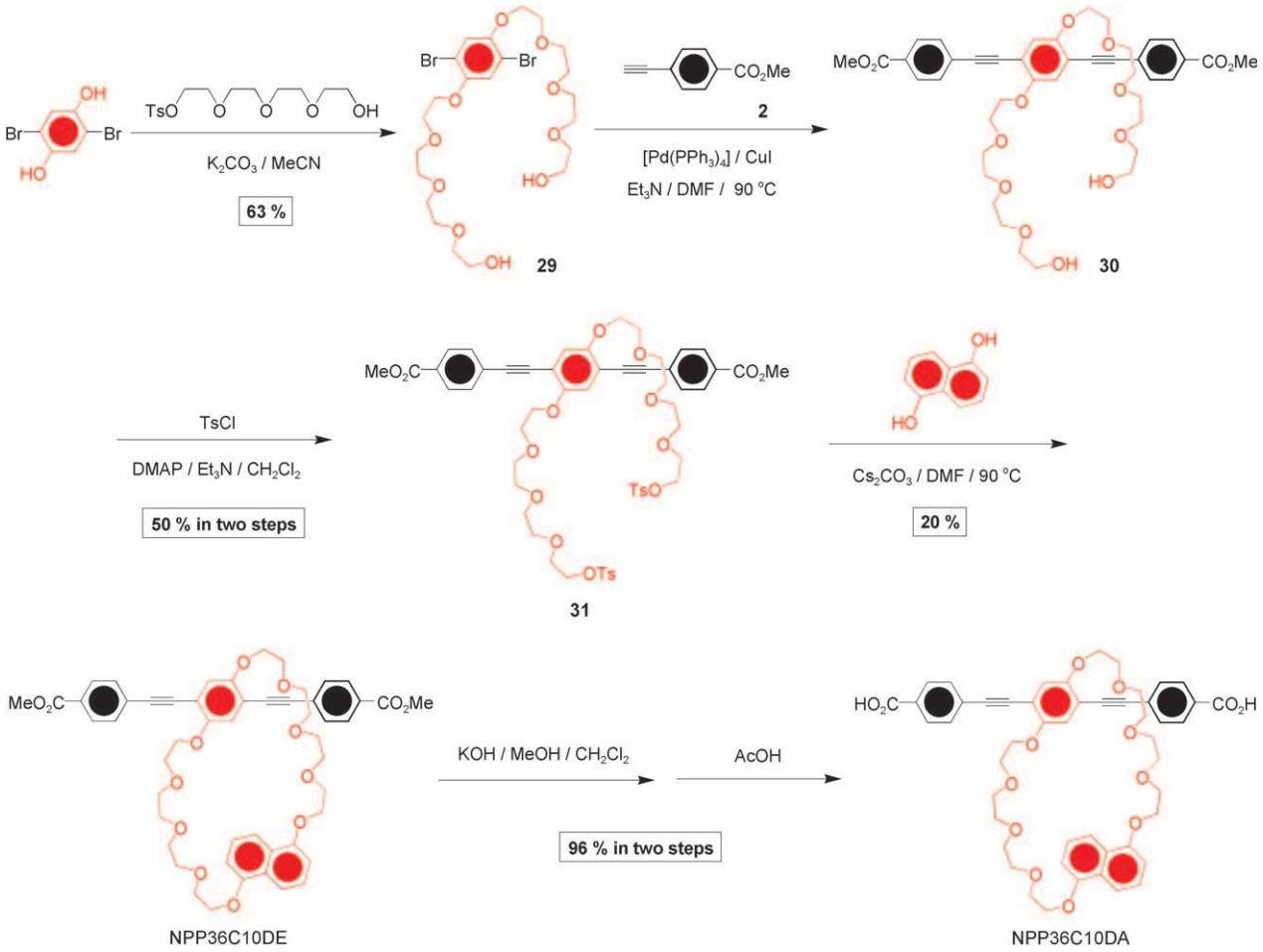

Scheme 7. The preparation of DN30C10DA.

hydroquinone moieties in the red lines) in $CD_3COCD_3$ at 200 K. In the $^1$H NMR spectra, the α, β, and methyl protons of the DMBP·2$PF_6$ guest shift upfield 0.20, 0.34, and 0.38 ppm (Table 1), respectively, upon complexation with BPP34C10DA in $CD_3COCD_3$ at 200 K, as a consequence of the shielding effect of the crown ether. The corresponding α, β, and methyl carbon nuclei shift upfield 0.5, 2.2, and 0.4 ppm (Table 1) under the same conditions, respectively. In the $^{15}$N NMR spectra, the uncomplexed DMBP·2$PF_6$ reveals a $^{15}$N signal centered at $\delta = 206.9$ ppm, and the signal shifts upfield to $\delta = 205.2$ ppm ($\Delta\delta = -1.7$ ppm) after complexation with BPP34C10DA. These NMR spectroscopic investigations confirm that the crown ether BPP34C10DA is capable of binding the $DMBP^{2+}$ dication, forming a host–guest complex.

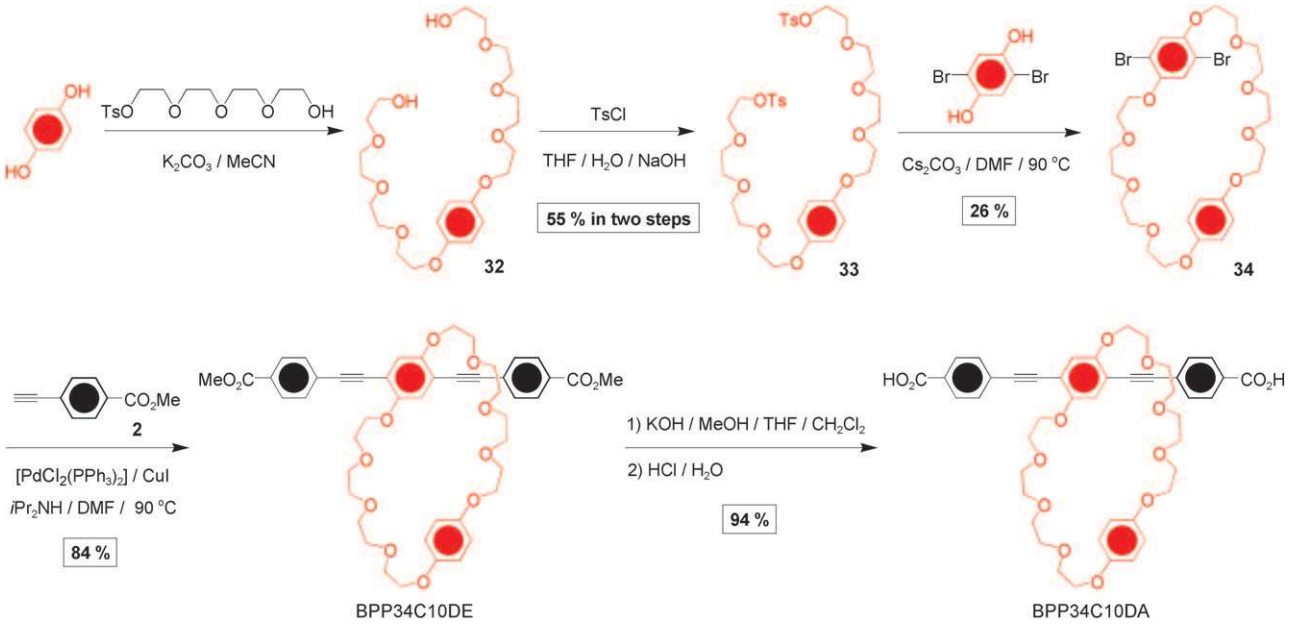
The signal splits of the α, β, and methyl protons in DMBP·2$PF_6$ upon complexation with BPP34C10DA were only observed at low temperatures, when the exchange of the complexed and uncomplexed DMBP·2$PF_6$ was slowed down on the NMR timescale. To investigate the dynamic behavior of the complex DMBP·2$PF_6$⊂BPP34C10DA, variable-temperature (VT) $^1$H NMR experiments of DMBP·2$PF_6$ ($1.2\times10^{-3}$ M) with BPP34C10DA ($4.0\times10^{-4}$ M) were carried out in $CD_3COCD_3$. Typically, the α, β, and methyl protons of DMBP·2$PF_6$ in the NMR spectra (Figure 2) at 217 K feature two broad peaks, respectively, which are assigned to the proton signal of the complexed and uncomplexed DMBP·2$PF_6$. Upon increasing the temperature to 298 K, these broad peaks coalesce into one peak. The protons in the crown ether BPP34C10DA show no obvious separation of the signals under the same conditions.

The protons in the [2]catenanes $H_2$NPP36C10DC-CAT·4$PF_6$, BPP34C10DE-CAT·4$PF_6$, and $H_2$BPP34C10DC-CAT·4$PF_6$ were assigned fully by $^1$H–$^1$H COSY experiments at 298 K. The VT $^1$H NMR experiments on the [2]catenanes were conducted to investigate the dynamics of the [2]catenanes, namely, the pirouetting of the cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) rings around the macrocycles. Since $H_2$BPP34C10DC-CAT·4$PF_6$ exhibits poor solubility, we employed its analogue, BPP34C10DE-CAT·4$PF_6$, to perform the VT NMR experiments in $CD_3COCD_3$. Partial VT $^1$H NMR spectra of BPP34C10DE-CAT·4$PF_6$ are shown in Figure 3 and the kinetic and thermodynamic parameters for the dynamic process observed in BPP34C10DE-CAT·4$PF_6$ are listed in Table 2. In the $^1$H NMR spectrum at 245 K, the α, β, and $CH_2$ protons on the $CBPQT^{4+}$ ring show mainly two, two, and three broad peaks, respectively. With increasing the temperature to 295 K, these broad peaks coalesce into one peak. These spectral changes correspond to the free energy of activations ($\Delta G_c^{\neq}$)[14] of 10.6 (α protons), 10.6 (β protons), and 10.5 ($CH_2$ protons) kcal mol$^{-1}$. The free energy values are found to be lower than that (12.0 kcal mol$^{-1}$) observed previously[15] for other $CBPQT^{4+}$ ring-based [2]catenane systems, probably because the introduc-

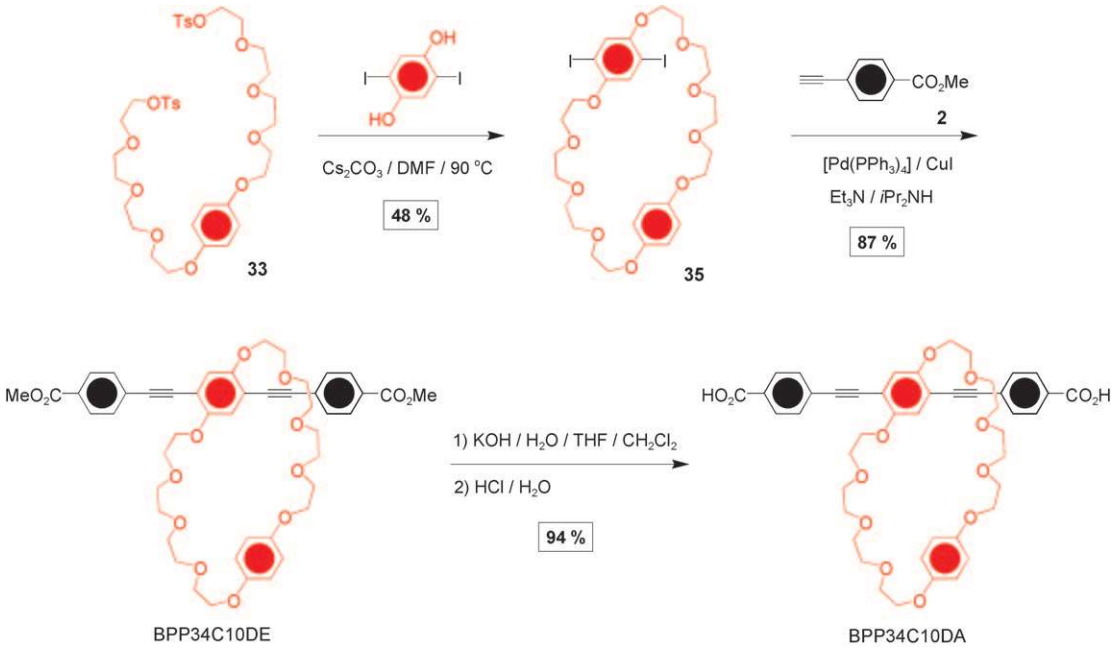



Scheme 8. The preparation of NPP36C10DA. DMAP = 4-dimethylaminopyridine, Ts = *p*-toluenesulfonyl.

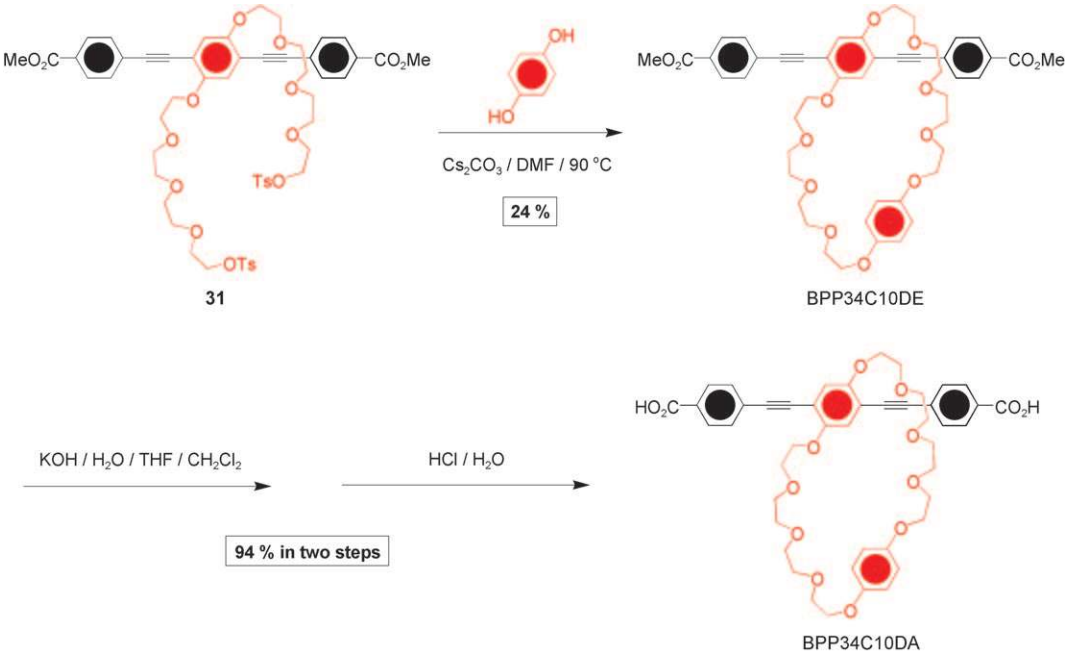



Scheme 9. The preparation of BPP34C10DA.




Scheme 10. The preparation of BPP34C10DA.

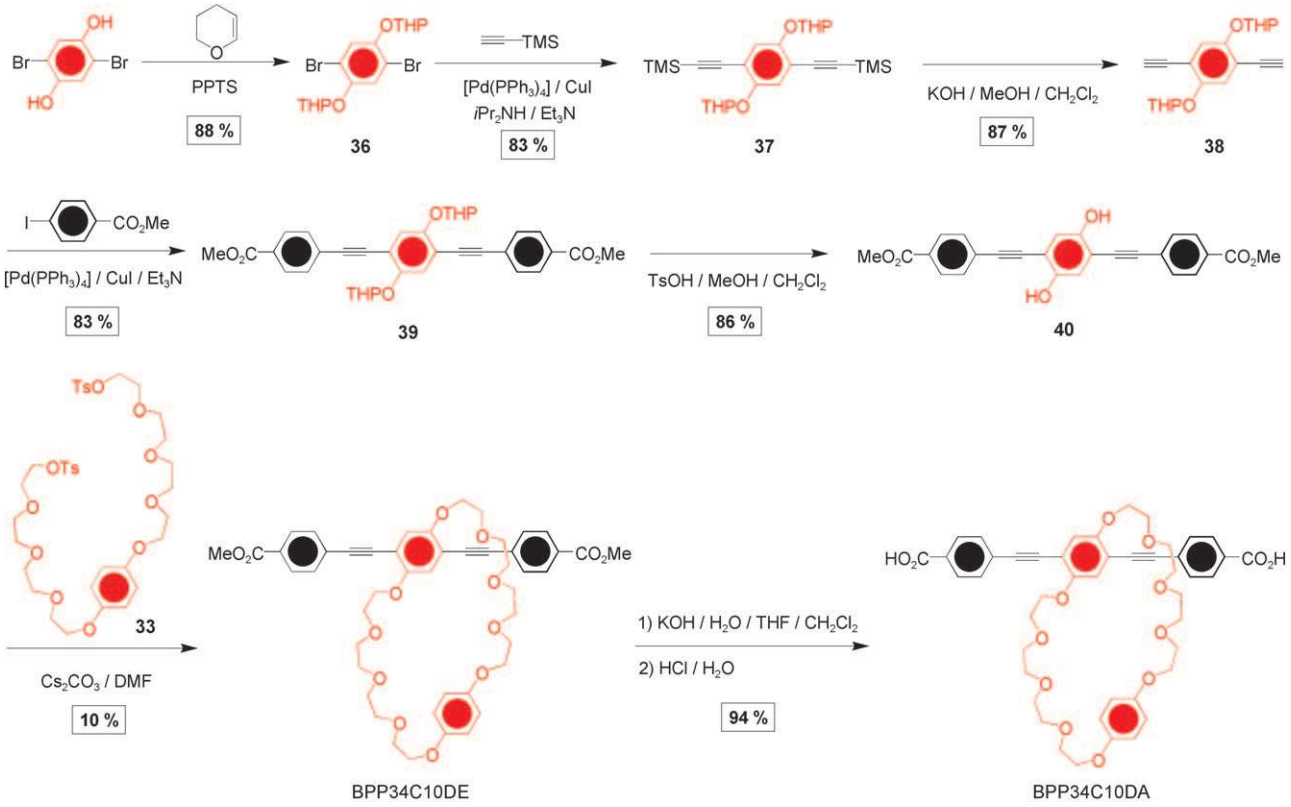



Scheme 11. The preparation of BPP34C10DA.

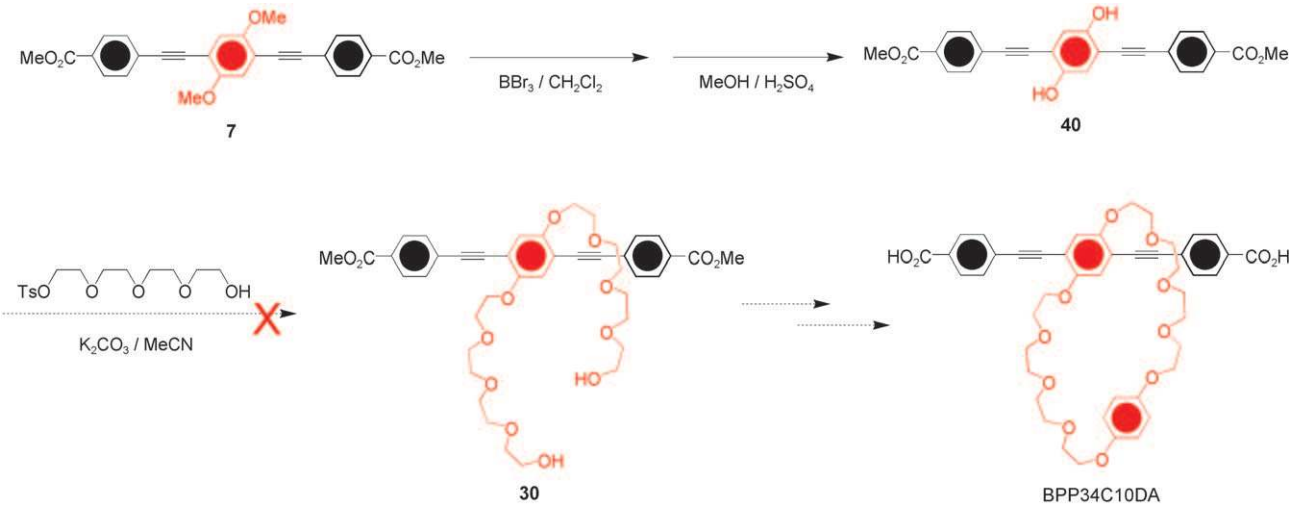
tion of the linearly rigid struts to the crown ethers limits efficient pirouetting of the CBPQT$^{4+}$ ring in the [2]catenanes.

**Crystal structures and geometrical analyses**: Direct evidence for the formation of good quality single crystals for **31**, BPP34C10DE, NPP36C10DA, DMBP·2$PF_6$⊂BPP34C10DA,[11] BPP34C10DE-CAT·4$PF_6$, MOF-1001,[11] and MOF-1002[11] has been obtained in the solid state. The crystal data and experimental and refinement parameters for these crystals are listed in Table 3. Single-crystal **31**, an important precursor for the rigid-strut-containing crown ethers, is monoclinic and has a space group of *P*21/*c*. In its crystal structure (Figure 4), two terminal phenylene rings in the methyl benzoate units are twisted with respect to the central hydroquinone ring (33° of dihedral angles between the terminal phenylene rings and the central hydroquinone




Scheme 12. The preparation of BPP34C10DA. PPTS = pyridinium *p*-toluenesulfonate.

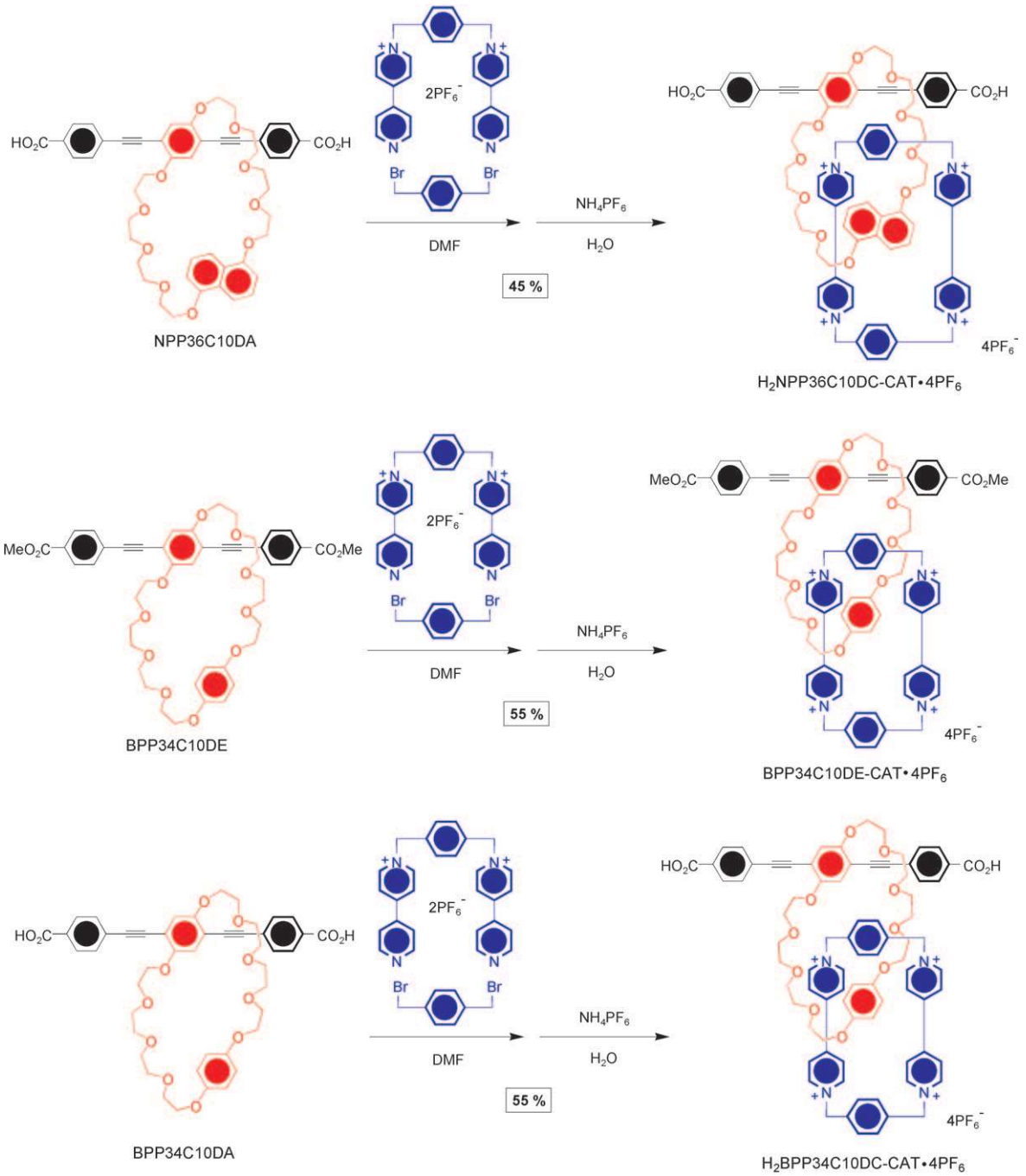



Scheme 13. The preparation of BPP34C10DA.

ring) on the fully rigid conjugated framework. Each of the tosylated diethyleneglycol chains in **31** adopts an S-shaped geometry. The packing structure of the compound **31** is stabilized by intermolecular π–π stacking interactions and hydrogen bonds between the oxygen atoms of the tetraethyleneglycol chains and the protons of the tosyl benzene rings in neighboring molecules, between the oxygen atoms of the sulfonyl groups and the protons of the tetraethyleneglycol chains in neighboring molecules, and between the oxygen atoms of the tetraethyleneglycol chains and the methyl protons of the methyl benzoate units in neighboring molecules.

The crystal structure of the crown ether BPP34C10DE is triclinic and has (Table 3) a space group of $P\bar{1}$. In common with **31**, two terminal phenylene rings in the methyl benzoate units are twisted with respect to the central hydroquinone ring (16 and 19° of dihedral angles between the termi-




Scheme 14. The syntheses of $H_2$NPP36C10DC-CAT·4 $PF_6$, BPP34C10DE-CAT·4 $PF_6$, and $H_2$BPP34C10DC-CAT·4 $PF_6$.

nal phenylene rings and the central hydroquinone ring, respectively) in the crystal structure of BPP34C10DE (Figure 5). The two hydroquinone rings in the crown ether are not parallel; they have a dihedral angle of 125°. The two hydroquinone rings have *anti* geometries associated with the conformation of the tetraethyleneglycol chains. The packing structure of the crystal BPP34C10DE may be stabilized by intermolecular hydrogen bonds between the oxygen and hydrogen atoms in the tetraethyleneglycol chains. The fact of the matter is that the rigid-strut-containing crown ethers BPP34C10DA, BPP34C10DE, NPP36C10DA, and NPP36C10DE have planar chirality, since they have no planes or centers of symmetry.[16] The planar chirality of the crown ethers can be demonstrated by their crystal structures. We note that both racemic *R* and *S* enantiomers are present in a 1:1 ratio in the crystal structure of BPP34C10DE (Figure 5).

The crystal structure of the crown ether NPP36C10DA is triclinic and has a space group of $P\bar{1}$ (Table 3). Two terminal phenylene rings in the benzoic acid units are twisted with re-

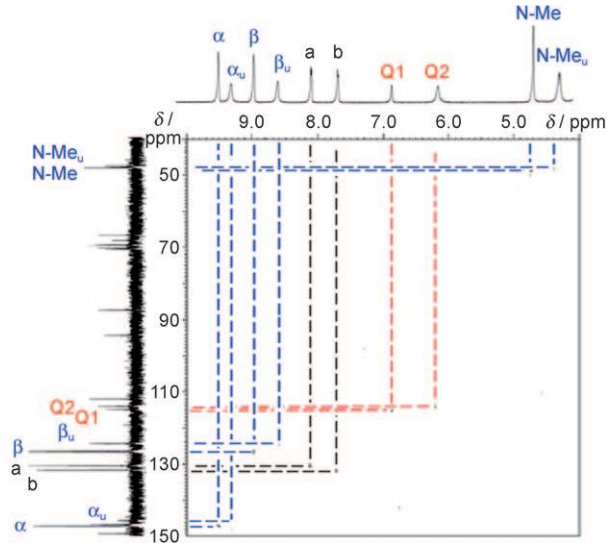



Figure 1. Partial $^{1}H$–$^{13}C$ HMQC spectrum of DMBP·2$PF_6$ ($1.2\times10^{-3}$ M) and BPP34C10DA ($4.0\times10^{-4}$ M) in $CD_3COCD_3$ at 200 K. The abscissa shows the $^{1}H$ NMR spectrum and the ordinate shows the $^{13}C$ NMR one. Correlations among nuclei in DMBP·2$PF_6$ (blue lines), and 4-carboxyphenylethynyl (black lines) and hydroquinone (red lines) moieties of BPP34C10DA are indicated in the spectrum. The nuclei in the complexed DMBP·2$PF_6$ label as α, β, and N-Me and these in the uncomplexed DMBP·2$PF_6$ label as $\alpha_u$, $\beta_u$, and N-$Me_u$. The nuclei are defined alongside their structural formulas.

Table 1. Changes of chemical shifts of selected nuclei in the complex ($\delta_c$) DMBP·2$PF_6$⊂BPP34C10DA ($1.2\times10^{-3}$ M) as compared to those of the uncomplexed ($\delta_u$) DMBP·2$PF_6$ ($1.2\times10^{-3}$ M) in $CD_3COCD_3$ at 200 K. $\Delta\delta$ is the chemical shift difference.

| Nuclei | $^{1}H$ | | | $^{13}C$ | | | $^{15}N$ |
|---|---|---|---|---|---|---|---|
| | α | β | N-Me | α | β | N-Me | N-Me |
| $\delta_u$ [ppm] | 9.50 | 8.96 | 4.72 | 147.1 | 126.7 | 48.5 | 206.9 |
| $\delta_c$ [ppm] | 8.96 | 8.62 | 4.34 | 146.6 | 124.5 | 48.1 | 205.2 |
| $\Delta\delta$ [ppm] | −0.20 | −0.34 | −0.38 | −0.5 | −2.2 | −0.4 | −1.7 |

spect to the central hydroquinone ring (16 and 157° of dihedral angles between the terminal phenylene rings and the central hydroquinone ring, respectively) in the crystal structure of NPP36C10DA (Figure 6). The 1,5-dihydroxynaphthalene unit and central hydroquinone ring in the crown ether are not parallel; they have a dihedral angle of 61°. The packing structure of the crystal NPP36C10DA is stabilized by intermolecular π–π stacking interactions and hydrogen bonds between the oxygen atoms of the carboxylic acid units and the protons of the tetraethyleneglycol chains in neighboring molecules, between the oxygen atoms of the tetraethyleneglycol chains and the protons of the central hydroquinone ring in neighboring molecules, and between the carboxylic acid groups in the adjacent molecules. NPP36C10DA displays its planar chirality with 1:1 racemic *R* and *S* enantiomers in the crystal structure.

The crystal superstructure of the complex DMBP·2$PF_6$⊂BPP34C10DA is triclinic and has a space group of $P\bar{1}$ (Table 3). The crystal superstructure (Figure 7)

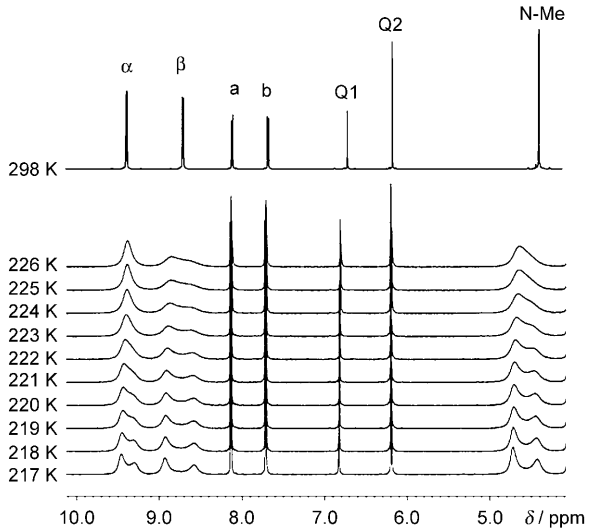



Figure 2. Partial $^{1}H$ NMR spectra of DMBP·2$PF_6$ ($1.2\times10^{-3}$ M) and BPP34C10DA ($4.0\times10^{-4}$ M) in $CD_3COCD_3$ at various temperatures. The exchange of the complexed and uncomplexed DMBP·2$PF_6$ was slowed down at low temperatures, leading to the splits of the α, β, and methyl proton signals in DMBP·2$PF_6$.

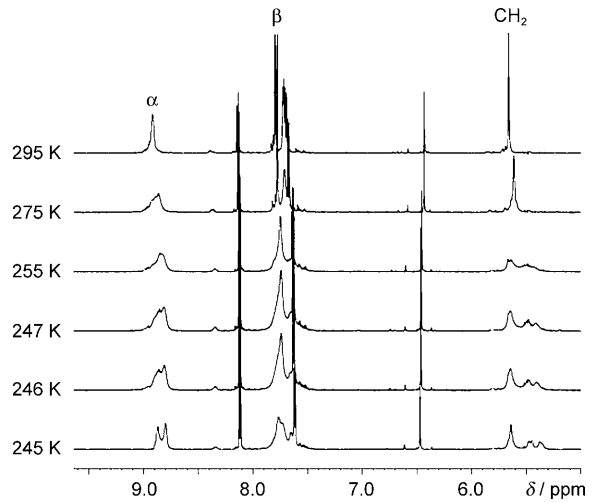



Figure 3. Partial VT $^{1}H$ NMR spectra of the [2]catenane BPP34C10DE-CAT·4$PF_6$ in $CD_3COCD_3$.

Table 2. Kinetic and thermodynamic parameters for the pirouetting process of $CBPQT^{4+}$ resonances in BPP34C10DE-CAT·4$PF_6$. $\Delta\nu$ is the chemical shift difference between the coalescing signals at low temperature in the absence of exchange. $k_c$ is calculated from the expression, $k_c=\pi(\Delta\nu)/2^{1/2}$. $T_c$ is the temperature of the spectrometer probe at coalescence. The Eyring equation was employed to calculate activation energy $\Delta G_c^{\ddagger}$.

| Probe protons | $\Delta\nu$ [Hz] | $k_c$ [$s^{-1}$] | $T_c$ [K] | $\Delta G_c^{\ddagger}$ [kcal $mol^{-1}$] |
|---|---|---|---|---|
| α | 42.3 | 92.9 | 251 | 10.6 |
| β | 24.5 | 52.8 | 245 | 10.6 |
| $CH_2$ | 136.0 | 300.7 | 262 | 10.5 |

shows clearly that the π-electron-deficient bipyridinium dication DMBP·2$PF_6$ is inserted through the middle of the

Table 3. Crystal data, experimental and refinement parameters for the crystals **31**, BPP34C10DE, NPP36C10DA, DMBP•2 $PF_6$⊂BPP34C10DA, and BPP34C10DE-CAT•4 $PF_6$.

| | **31** | BPP34C10DE | NPP36C10DA | DMBP•2 PF6⊂BPP34C10DA | BPP34C10DE-CAT•4 PF6 |
|---|---|---|---|---|---|
| molecular formula | $C_{56}H_{62}O_{18}S_2$ | $C_{48}H_{52}O_{14}$ | $C_{56}H_{64}O_{15}$ | $C_{65.5}H_{76}F_{12}N_2O_{16.5}P_2$ | C94H101F24N9O15P4 |
| $M_r$ [g mol$^{-1}$] | 1087.18 | 852.90 | 977.07 | 1446.22 | 2176.72 |
| $T$ [K] | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| $\lambda$ [Å] | 0.71073 | 1.54178 | 0.71073 | 1.54178 | 0.71073 |
| crystal system | monoclinic | triclinic | triclinic | triclinic | monoclinic |
| space group | $P21/c$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P21/n$ |
| $a$ [Å] | 8.1408(3) | 9.0342(3) | 9.52(8) | 11.0078(4) | 13.654(3) |
| $b$ [Å] | 10.1129(4) | 13.5428(5) | 13.34(11) | 16.9569(6) | 29.947(6) |
| $c$ [Å] | 32.1022(14) | 18.2351(6) | 21.27(18) | 19.1579(7) | 24.499(5) |
| $\alpha$ [°] | 90 | 81.512(2) | 101.73(7) | 73.836(2) | 90 |
| $\beta$ [°] | 96.582(3) | 77.525(2) | 98.67(7) | 83.257(2) | 96.253(2) |
| $\gamma$ [°] | 90 | 83.614(2) | 97.67(7) | 85.681(2) | 90 |
| $V$ [Å$^3$] | 2625.46 | 2147.22(13) | 2576.73 | 3407.5(2) | 9958(4) |
| $Z$ | 2 | 2 | 2 | 2 | 4 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.375 | 1.319 | 1.259 | 1.409 | 1.452 |
| $\mu$ ($Mo_{K\alpha}$) [mm$^{-1}$] | 0.178 | 0.802 | 0.091 | 1.469 | 0.188 |
| $F$(000) | 1148 | 904 | 1040 | 1506 | 4496 |
| crystal size [mm$^3$] | 0.41×0.33×0.02 | 0.36×0.17×0.13 | 0.35×0.20×0.10 | 0.10×0.10×0.05 | 0.40×0.20×0.15 |
| $\theta$ range for data collection [°] | 2.11–30.56 | 2.50–48.82 | 2.25–32.47 | 2.41–43.99 | 3.79–28.26 |
| index ranges | $-11 \le h \le 11$ | $-8 \le h \le 8$ | $-13 \le h \le 11$ | $-9 \le h \le 9$ | $-18 \le h \le 18$ |
| | $-14 \le k \le 13$ | $-13 \le k \le 12$ | $-18 \le k \le 18$ | $-15 \le k \le 15$ | $-39 \le k \le 39$ |
| | $-45 \le l \le 45$ | $-16 \le l \le 17$ | $-30 \le l \le 30$ | $-16 \le l \le 17$ | $-32 \le l \le 32$ |
| no. of reflns collected | 30395 | 8826 | 23120 | 9915 | 87664 |
| no. of unique reflns | 7898 | 3697 | 13940 | 4650 | 24449 |
| $R_{int}$ | 0.2830 | 0.0226 | 0.4304 | 0.0554 | 0.0708 |
| data/restraints/parameters | 7898/0/345 | 3697/0/561 | 13940/0/647 | 4650/65/620 | 24449/0/1381 |
| goodness-of-fit on $F^2$ | 0.815 | 1.042 | 0.721 | 1.061 | 1.020 |
| $R_1$ ($I > 2\sigma$ ($I$)) | 0.0696 | 0.0348 | 0.0994 | 0.0961 | 0.0708 |
| $wR_2$ (all data) | 0.1610 | 0.0891 | 0.2847 | 0.2525 | 0.2057 |
| $\Delta\rho$ max/min [e Å$^{-3}$] | 0.381/−0.419 | 0.198/−0.160 | 0.481/−0.294 | 0.771/−0.447 | 0.785/−0.724 |

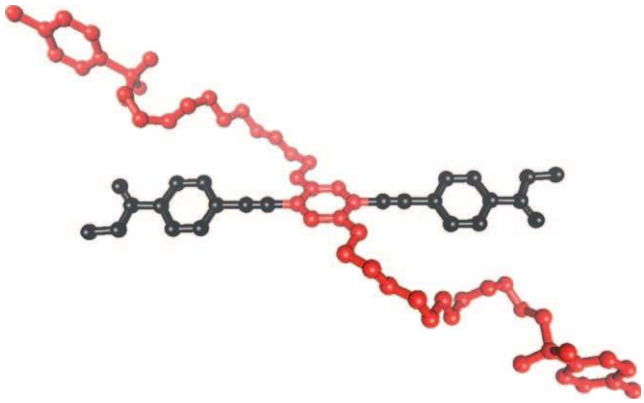


Figure 4. The crystal structure of **31**. The hydrogen atoms are omitted for the sake of clarity. Tetraethyleneglycol chains, tosyl units, and central hydroquinone ring are colored red and the rest is colored black.

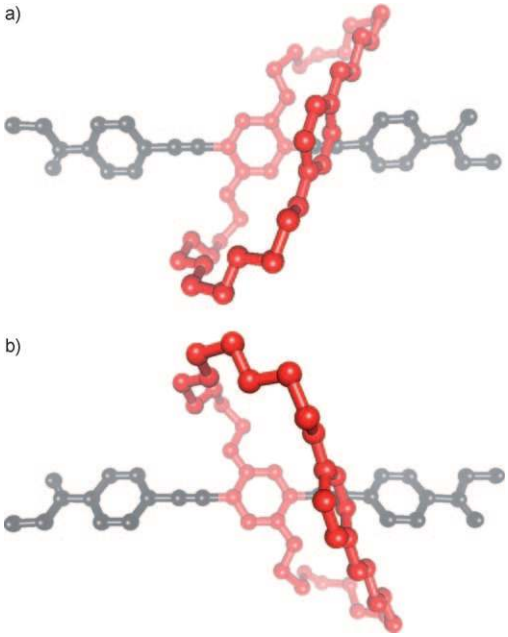



Figure 5. a) Side view of the *R* isomer and b) side view of the *S* isomer for the crystal structure of the crown ether BPP34C10DE. The hydrogen atoms are omitted for the sake of clarity. Tetraethyleneglycol chain and hydroquinone rings are colored red and the rest is colored black.

macrocyclic ring, forming a 1:1 host–guest complex. The two terminal methylene groups of DMBP•2 $PF_6$ protrude above and below the periphery of the macrocyclic ring, respectively, in a pseudorotaxane-like manner. The interplanar separation between the bipyridinium ring in DMBP•2 $PF_6$ and each hydroquinone ring is approximately 3.7 Å. This host–guest geometry is similar to that in the crystal superstructure[6] of the 1:1 complex between the crown ether BPP34C10 and DMBP•2 $PF_6$. The DMBP•2 $PF_6$⊂BPP34C10DA complex is stabilized by weak π–π stacking interactions between the bipyridinium ring and the two hydroquinone rings (4 and 11° of dihedral angles between the bipyridinium ring and the

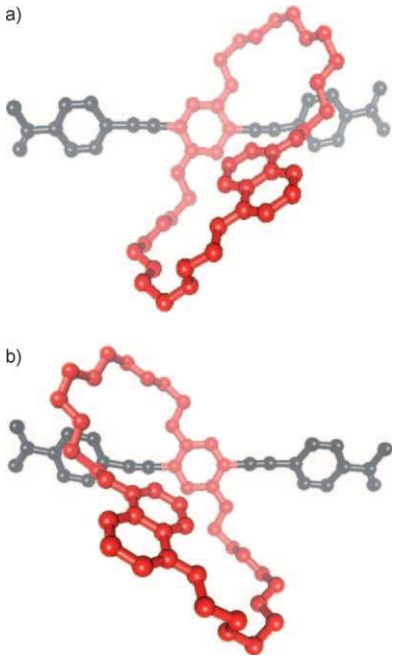



Figure 6. a) Side view of the *R* isomer and b) side view of the *S* isomer for the crystal structure of the crown ether NPP36C10DA. The hydrogen atoms are omitted for the sake of clarity. Tetraethyleneglycol chain, 1,5-dihydroxynaphthalene ring, and central hydroquinone ring are colored red and the rest is colored black.

two hydroquinone rings, respectively), and C–H···O hydrogen bonds between the oxygen atoms of the tetraethyleneglycol chains and the α protons of the bipyridinium ring in DMBP•2 $PF_6$ and between the oxygen atoms of the tetraethyleneglycol chains and the methyl protons of DMBP•2 $PF_6$. Two terminal phenylene rings in the benzoic acid units are twisted with respect to the central hydroquinone ring (33 and 32° of dihedral angles between the terminal phenylene rings and the central hydroquinone ring, respectively) in the crystal superstructure. Unlike the crystal structures of the crown ethers BPP34C10DE and NPP36C10DA, the two hydroquinone rings in the crown ether BPP34C10DA are parallel each other, with a dihedral angle of 2°, to render the π–π stacking interactions with the DMBP•2 $PF_6$ guest. The central hydroquinone ring on the rigid strut has an *anti* geometry associated with the conformation of the tetraethyleneglycol chains, whereas the other hydroquinone ring adopts a *syn* geometry. In the packing structure of the complex, intermolecular π–π stacking interactions and the hydrogen-bond network formed by the host and guest molecules and intervening solvent molecules and counterions extend the complexes to a higher architectural level. The complex DMBP•2 $PF_6$⊂BPP34C10DA also shows (Figure 7) the presence of *R* and *S* enantiomers with a 1:1 ratio in the crystal superstructure.

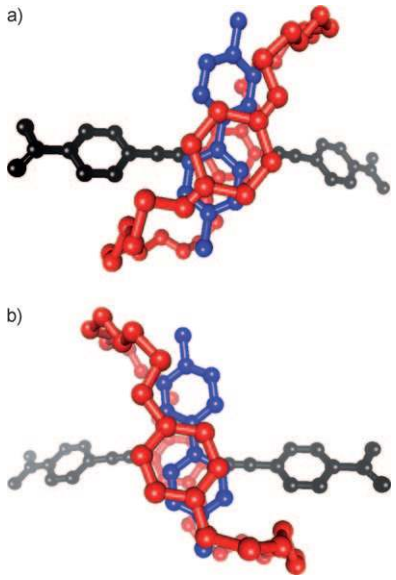



Figure 7. a) Side view of the *R* isomer and b) top view of the *S* isomer for the crystal superstructure of the complex $DMBP^{2+}$⊂BPP34C10DA. Hydrogen atoms, solvent molecules, and counterions are omitted for the sake of clarity. Tetraethyleneglycol chains and two hydroquinone rings are colored red, $DMBP^{2+}$ is colored blue, and the rest is colored black.

The crystal structure of the [2]catenane BPP34C10DE-CAT•4 $PF_6$ is monoclinic and has a space group of *P*21/*n* (Table 3). There are both *R* and *S* isomers (Figure 8) with a 1:1 ratio present in the crystal cell, in keeping with the planar chirality of the [2]catenane. For each isomer, the crystal structure of the [2]catenane BPP34C10DE-CAT•4 $PF_6$ reveals alternating π-donor/π-acceptor stacking interactions as a consequence of the threading of the BPP34C10DE macrocycle through the inside of the $CBPQT^{4+}$ ring. One hydroquinone ring is inside and the other is alongside the $CBPQT^{4+}$ ring, while one bipyridinium unit is inside and the other is alongside the BPP34C10DE macrocycle. The mean plane separations of 7.1 Å between the two hydroquinone rings in BPP34C10DE and of 7.1 Å between the two bipyridinium rings equate with interplanar separations of approximately 3.5 Å between the π donors and acceptors.[6] The [2]catenane is stabilized by weak π–π stacking interactions between the alternating bipyridinium rings and the hydroquinone rings and C–H···O hydrogen bonds between the oxygen atoms of the tetraethyleneglycol chains and the α protons of the bipyridinium ring inside the macrocycle and between the oxygen atoms of the tetraethyleneglycol chains and the methylene protons of the $CBPQT^{4+}$ ring. The values for the twist angles ($\theta$) and for other angles ($\psi$ and $\phi$) associated with the bowing of the aromatic residues in the $CBPQT^{4+}$ ring are similar to the values reported[6] previously for the BPP34C10/$CBPQT^{4+}$ [2]catenane. Both the hydroquinone rings have an *anti* geometry associated with the conformation of the tetraethyleneglycol chains. Two terminal phenylene rings in the methyl benzoate units are twisted with respect to the central hydroquinone ring (21 and 12° of dihedral angles between the terminal phenylene rings and the central hydroquinone ring, respectively) in the crystal structure. In the packing structure of the [2]catenane, intermolecular π–π stacking interactions and the hydrogen-bond network associated with

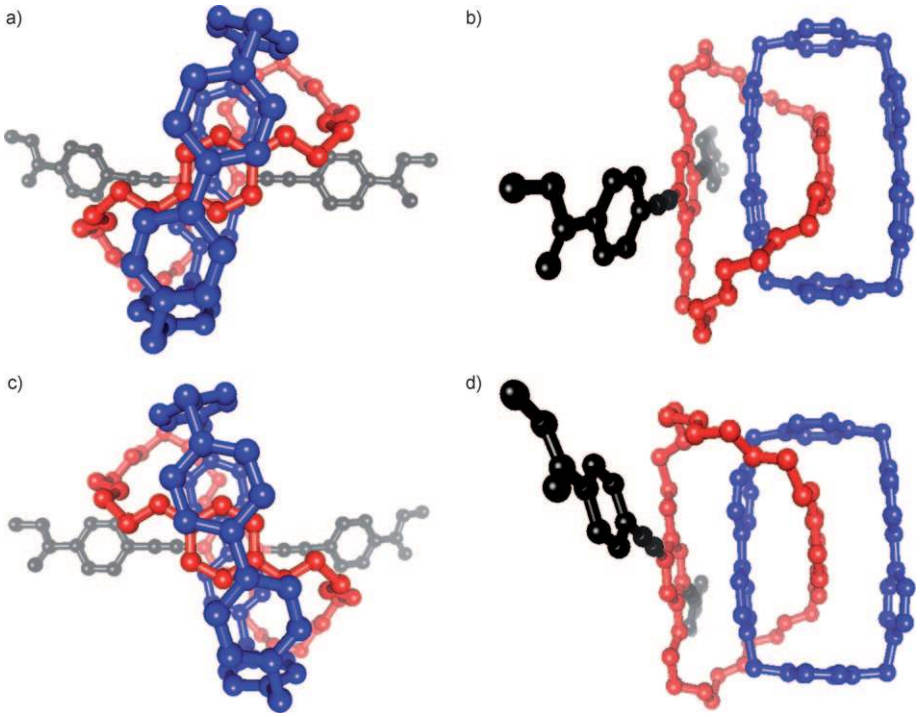



Figure 8. The crystal structure of the [2]catenane BPP34C10DE-CAT$^{4+}$: a) side view of the *R* isomer, b) top view of the *R* isomer, c) side view of the *S* isomer, and d) top view of the *S* isomer. Hydrogen atoms, solvent molecules, and counterions are omitted for the sake of clarity. Tetraethyleneglycol chain and two hydroquinone rings are colored red, the CBPQT$^{4+}$ ring is colored blue, and the rest is colored black.

the alternating *R*/*S* isomers and intervening solvent molecules and counterions extend the [2]catenanes to a higher architectural level.

The crystals of MOF-1001 and MOF-1002 were prepared in the oven isothermally. Bulk purities of MOF-1001 and MOF-1002 were characterized by elemental analysis, powder X-ray diffraction, and solid-state $^{13}C$ NMR spectroscopy. The crystals MOF-1001 and MOF-1002 (Figure 9) are cubic with $Fm\bar{3}m$ symmetry. The length of an edge (strut and metal oxide) in MOF-1001 and MOF-1002 cubes is approximately 26.5 Å, making them the largest in the crystalline non-interpenetrating isoreticular MOF series.[10] Single-crystal X-ray diffraction investigations indicate that MOF-1002 shares an identical cubic backbone with MOF-1001, affirming the generality of such synthetic methodology for building a variety of crystalline structures with complexity. Crystal data for MOF-1001 are $C_{72}H_{36}O_{13}Zn_4$, $M_r = 1370.49$, $a = 52.9345(7)$ Å, $V = 148326(3)$ Å$^3$, $\rho_{calcd} = 0.123\ g\,cm^{-3}$, $\lambda = 1.54178$ Å, $Z = 8$, reflections: 57237, independent reflections: 1508, $R_1$ $(I > 2\sigma(I)) = 0.0820$, $wR_2$ (all data) $= 0.2588$, and GOF $= 1.042$. To prove the correctness of the atomic positions in the framework, the application of the SQUEEZE[17] routine of Spek has been performed with the backbone framework only. If all the atoms in the framework are considered, the calculated empirical formula is $C_{138}H_{138}O_{43}Zn_4$ with a density of $0.246\ g\,cm^{-3}$.[11] Atomic coordinates of MOF-1002 were simulated based on the structure of MOF-1001.[11] 986 reflections with min. $I/\sigma$ 20 were harvested for unit cell determination of MOF-1002 from a total of 240 frames. The $\theta$ range for the unit cell determination is 2.350–37.375°. The Bravis lattice of cubic *F* with $a = 52.9482$ Å was chosen. In the crystal structures of the MOFs, solvent molecules exist as guests inside the pores. The crown ether struts BPP34C10DA and NPP36C10DA in MOFs present planar chirality with equal numbers of *R* and *S* enantiomers, that is, the extended structures are racemic with respect to the planes of chirality generated at the hyrdoquinone ring, incorporating both the struts and the crown ethers. Two carboxylate groups of the crown ether strut BPP34C10DA or NPP36C10DA were coordinated with $Zn^{2+}$ joints to afford the cubic structures. In each cube (Figure 9), eight $Zn_4O(CO_2)_6$ serve as the joints of the cube and twelve free macrocy-

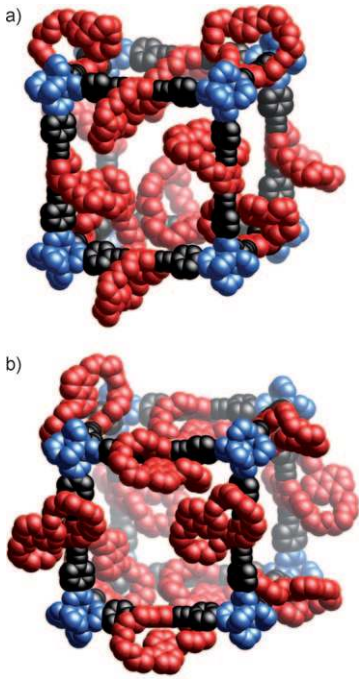



Figure 9. Space-filling representation of the crystal structures of a) MOF-1001 and b) MOF-1002. Hydrogen atoms and solvent molecules are omitted for the sake of clarity. Crown ether units with tetraethyleneglycol chain and two hydroquinone rings are colored red, the rigid struts are colored black, and the metal joints are colored blue.

cles are anchored in the edges of the cube. Based on the overall geometries and stoichiometries of the frameworks, it can be concluded that the rigid-strut-containing crown ethers can be integrated precisely and periodically into the robust frameworks of MOFs. Thus, the extended frameworks provide excellent scaffolding for expressing recognition sites in three-dimensional space.

## Conclusion

Sonogashira couplings are central to the general approaches developed in this research directed toward the synthesis of dicarboxylic acid terminated rigid struts, incorporating the aromatic crown ethers DB30C10, DN30C10, BPP34C10, and NPP36C10, which we have identified as DB30C10DA, DN30C10DA, BPP34C10DA, and NPP36C10DA prior to their incorporation into metal–organic frameworks. During the course of the synthesis of the dicarboxylic acids, we became aware of the planar chirality associated with the *para*-disubstituted hydroquinone rings in BPP34C10DA and NPP36C10DA. It has not escaped our attention that derivatives of these particular crown ethers, provided the struts are sufficiently long to prevent their passing through the middle of the macrocyclic polyethers, could be obtained as optically active compounds either 1) following their resolution in bulk quantities by classical methods, or 2) after separation of enantiomers on chiral high-performance liquid chromatography columns, or 3) by carrying out asymmetric Sonogashira couplings[9h] to generate the planar prochirality enantioselectively in the paracyclophane-like crown ether struts during their synthesis.

The synthetic work described herein establishes that the necessary strut precursors with symmetrically located crown ether receptors can be prepared in sufficiently large quantities, so that they can be employed subsequently in the preparation of metal–organic frameworks containing active domains, namely, recognition sites for particular substrates, for example, the paraquat dication. There is also every prospect of being able to prepare homochiral extended structures in which the source of the handedness in the struts is that of planar chirality.

## Experimental Section

**General**: All reagents were purchased and used without further purification. Thin-layer chromatography (TLC) was performed on glass plates, precoated with silica gel 60 with fluorescent indicator. The plates were inspected by UV light. Column chromatography was carried out on silica gel 60F. UV/Vis spectroscopy was performed on an Agilent 8453 spectrophotometer system at 25 °C. Emission spectra were recorded on a coupled charge device (CCD) through a SpectraPro 2300i 0.300 m imaging Triple Grating monochromator/spectrograph, excited by a 377 nm/16 mW laser. NMR spectra were recorded on a Bruker ARX500 (500 MHz), DRX500 (500 MHz), or AV600 (600 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from the $Me_4Si$ resonance, which was used as the internal standard when recording NMR spectra. High-resolution matrix-assisted laser desorption/ionization spectra (HR-MALDI) were obtained on an AppliedBiosystems DE-STR MALDI time-of-flight mass spectrometer. The reported molecular mass ($m/z$) values were the most abundant monoisotopic mass. High-resolution electrospray ionization (ESI) mass spectra were measured on a Micromass Q-Tof Ultima (SCS, University of Illinois). The X-ray intensity data collected either on a Bruker SMART APEXII three circle diffractometer equipped with a CCD area detector and operated at 1200 W power (40 kV, 30 mA) to generate $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å) or equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The incident X-ray beam was focused and monochromated by using a Bruker Excalibur Gobel mirror optic.

**Compound 1**:[12] Methyl 4-iodobenzoate (15.7 g, 60.0 mmol), [$PdCl_2(PPh_3)_2$] (2.10 g, 2.99 mmol), CuI (0.11 g, 0.58 mmol), $i$$Pr_2NH$ (90 mL), and $Et_3N$ (200 mL) were added to a three-necked flask equipped with a condenser and a magnetic stirrer, and supplied with an inert atmosphere. The mixture was purged with Ar flow with stirring for 30 min and then trimethylsilylacetylene (2.78 g, 28.3 mmol) was added. The reaction mixture was slowly heated to 80 °C and stirred for 8 h at this temperature. After cooling to room temperature, the reaction mixture was filtered to remove insoluble materials, and the solid was washed with $CH_2Cl_2$. The filtrates were combined and the solvents were removed under reduced pressure to afford a yellowish orange residue, which was extracted with $CH_2Cl_2$ (500 mL). The organic layer was washed twice with $H_2O$ and dried ($MgSO_4$), before removing the solvent to give compound **4** (13.3 g, 95 %) as a yellow powder. It was pure enough to be employed directly in the next reaction. $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 0.26$ (s, 9H), 3.91 (s, 3H), 7.50–7.52 (d, $J = 8.7$ Hz, 2H), 7.95–7.97 ppm (d, $J = 8.3$ Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 0.0$, 52.1, 97.6, 104.0, 127.7, 129.3, 129.6, 131.8, 166.4 ppm.

**Compound 3**:[18] Ethyl 4-bromobenzoate (2.00 g, 8.73 mmol) was dissolved in DMF (80 mL) and $i$$Pr_2NH$ (20 mL). Under Ar protection, trimethylsilylacetylene (1.29 g, 13.1 mmol), [$Pd(PPh_3)_4$] (0.50 g, 0.44 mmol), and CuI (0.04 g, 0.44 mmol) were added to the solution. The mixture was then stirred under Ar at 80 °C for 48 h. The solvent was then removed in vacuo. The residue was dissolved in $CH_2Cl_2$ (50 mL) before being washed with $H_2O$ ($2 \times 20$ mL) and brine (20 mL). The organic phase was then dried ($Na_2SO_4$). After the solvent was removed in vacuo, column chromatography ($SiO_2$: hexane/$CH_2Cl_2 = 3:1$) was carried out to provide the product **3** as a yellow solid (2.03 g, 94 %). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 0.26$ (s, 9H; $Si(CH_3)_3$), 1.37–1.40 (t, $J = 7.1$ Hz, 3H; $CH_3$), 4.36–4.38 (q, $J = 7.1$ Hz, 2H; $CH_2$), 7.50–7.52 (d, $J = 8.7$ Hz, 2H; Ar-H), 7.76–7.78 ppm (d, $J = 8.7$ Hz, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$,): $\delta = 0.20$, 14.7, 61.5, 98.0, 104.5, 128.0, 129.7, 130.4, 132.2, 166.4 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{14}H_{19}O_2Si^+$ $[M+H]^+$: 247.1149; found: 247.1147.

**Compound 2**:[12] Compound **1** (0.81 g, 3.49 mmol) was dissolved in a mixture of MeOH (50 mL) and $CH_2Cl_2$ (50 mL), and $K_2CO_3$ (2.42 g, 17.5 mmol) was added. The reaction mixture was purged with Ar flow for 15 min and stirred at room temperature for 2 h. Most of solvents were removed under reduced pressure and $H_2O$ (50 mL) was added to the reaction mixture. The mixture was extracted with $Et_2O$ ($2 \times 50$ mL), and then the combined organic extracts were washed with brine ($3 \times 50$ mL). The combined organic extracts were then dried ($Na_2SO_4$) and filtered, and the solvent was evaporated in vacuo. Column chromatography ($SiO_2$: hexane/$CH_2Cl_2 = 3:1$) was carried out to afford the product **2** as a white solid (0.53 g, 95 %). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 3.23$ (s, 1H; C≡CH), 3.92 (s, 3H; $OCH_3$), 7.53–7.55 (d, $J = 8.7$ Hz, 2H; Ar-H), 7.96–7.99 ppm (d, $J = 8.7$ Hz, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 52.1$, 79.9, 82.7, 126.6, 129.3, 130.0, 131.9, 166.3 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{10}H_9O_2^+$ $[M+H]^+$: 161.0597; found: 161.0590. Compound **2** was also prepared from **3** as follows: $K_2CO_3$ (0.43 g, 3.04 mmol) was added to a solution of **3** (0.25 g, 1.01 mmol) in MeOH (10 mL) and the solution was stirred at room temperature for 2 h. The solid material was removed by filtration and the solvent was removed in vacuo. The residue was then dissolved in $CH_2Cl_2$ (5 mL) before being washed with $H_2O$ ($2 \times 3$ mL) and brine (3 mL). The organic phase was then dried ($Na_2SO_4$). After the solvent was removed in vacuo, column

chromatography ($SiO_2$: hexane/$CH_2Cl_2$ = 3:1) was carried out to afford the product **2** as a white solid (0.18 g, 99%).

**Compound 4**:[19] ICl (175 g, 1.08 mol) was added dropwise to MeOH (300 mL) below 15°C. 1,4-Dimethoxybenzene (34.5 g, 0.25 mol) was added to the mixture below 15°C and then the reaction mixture was heated under reflux for 4 h. After cooling the reaction mixture to room temperature, the resulting crystals were collected by filtration. The crystals were rinsed with cold MeOH and air dried to give the product **4** (84.0 g, 84%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.82 (s, 6H; $OCH_3$), 7.19 ppm (s, 2H; Ar-H).

**Compound 5**:[20] 1,4-Diiodo-2,5-dimethoxybenzene **4** (18.0 g, 46.0 mmol), [$Pd(PPh_3)_4$] (1.05 g, 0.92 mmol), CuI (0.35 g, 1.84 mmol), and $Et_3N$ (200 mL) were added to a three-necked flask equipped with a condenser and a magnetic stirrer under an inert atmosphere. The mixture was purged with an Ar flow with stirring for 30 min before trimethylsilylacetylene (13.9 g, 142 mmol) was added. The reaction mixture was slowly heated to 80°C and stirred for 8 h at this temperature. After cooling to room temperature, the insoluble material was collected by filtration and then rinsed with $CH_2Cl_2$ (650 mL). The solution in $CH_2Cl_2$ was combined with the filtrate and the organic phase was washed with $H_2O$ (2× 200 mL), and dried ($MgSO_4$). The solvent was removed in vacuo and the product **5** was collected as a white solid (14.2 g, 93%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 0.25 (s, 18H; $Si(CH_3)_3$), 3.81 (s, 6H; $OCH_3$), 6.89 ppm (s, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 0.4, 56.8, 101.2, 113.8, 116.6, 154.6 ppm; MS (ESI-TRAP): *m*/*z*: 330.14 $[M]^+$.

**Compound 6**:[21] $K_2CO_3$ (15.0 g, 108 mmol) was added to a solution of **5** (4.55 g, 13.7 mmol) in a mixture of $CH_2Cl_2$ (150 mL) and MeOH (150 mL). The reaction mixture was stirred for 4 h at room temperature. Most of the solvent was removed in vacuo and then $H_2O$ (300 mL) was added to the reaction mixture. A yellow suspension formed. The product **6** was collected by filtration and washed with $H_2O$ and MeOH (2.50 g, 98%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.37 (s, 2H; C≡CH), 3.84 (s, 6H; $OCH_3$), 6.96 ppm (s, 2H; Ar-H); MS (ESI-TRAP): *m*/*z*: 186.04 $[M]^+$.

**Compound 7**: Methyl 4-iodobenzoate (10.5 g, 40.0 mmol), [$Pd(PPh_3)_4$] (0.46 g. 0.40 mmol), and CuI (0.16 g, 0.80 mmol) were added to a mixture of *i*$Pr_2NH$ (15 mL) and DMF (100 mL). The mixture was purged with Ar while stirring for 30 min before a solution of **6** (3.70 g, 20.0 mmol) in DMF (40 mL) was slowly added. The reaction mixture was stirred for 8 h at 80°C. After cooling to room temperature, the insoluble material was collected by filtration, and washed with $H_2O$ (350 mL) and MeOH (100 mL). The yellow solid was dissolved in $CHCl_3$ (1200 mL), washed with $H_2O$ (300 mL), and dried ($MgSO_4$). The solvent was removed in vacuo to afford the product **7** (8.38 g, 92%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.91 (s, 6H; $OCH_3$), 3.93 (s, 6H; $COOCH_3$), 7.04 (s, 2H; Ar-H), 7.61–7.63 (d, *J* = 8.4 Hz, 4H; Ar-H), 8.01–8.04 ppm (d, *J* = 8.4 Hz, 4H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 52.1, 56.4, 88.4, 94.3, 113.2, 115.5, 127.7, 129.4, 129.5, 131.5, 153.9, 166.4 ppm; HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{23}O_6^+$ $[M+H]^+$: 455.1489; found: 455.1492.

**Compound 8**: **7** (1.00 g, 2.20 mmol) and NaOH (0.35 g, 8.80 mmol) were dissolved in a mixture of THF (50 mL) and $H_2O$ (50 mL). The solution was stirred at room temperature overnight. The pH of the solution was then adjusted to 2 with aqueous HCl solution (1 M). A precipitate formed, which was collected by filtration, washed with $H_2O$, and dried in air to afford the product **8** (0.92 g, 98%). $^1$H NMR (500 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 3.87 (s, 6H; $OCH_3$), 7.25 (s, 2H; Ar-H), 7.65–7.67 (d, *J* = 8.5 Hz, 4H; Ar-H), 7.97–7.99 (d, *J* = 8.5 Hz, 4H; Ar-H), 13.18 ppm (s, 2H; COOH); $^{13}$C NMR (125 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 56.7, 89.0, 94.4, 112.8, 116.0, 127.0, 129.9, 131.0, 131.8, 154.0, 167.9 ppm; HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{19}O_6^+$ $[M+H]^+$: 427.1176; found: 427.1176.

**Compound 9**: A solution of $Br_2$ (40.6 g, 124 mmol) in AcOH (65 mL) was gradually added to a stirred solution of naphthalene-2,3-diol (20.0 g, 124 mmol) in AcOH (85 mL). The reaction mixture was stirred overnight at room temperature to form a white suspension. The solid was filtered, washed with $H_2O$ (300 mL), and dried in air. The product **9** was purified by recrystallization from $CHCl_3$ (32.0 g, 81%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 6.17 (s, 2H; OH), 7.51–7.53 (d, 2H; Ar-H), 8.07–8.09 ppm (d, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 107.3, 125.1, 125.8, 128.8, 148.5 ppm; MS (ESI-TRAP): *m*/*z*: 315.90 $[M]^+$.

**Compound 10**: A solution of *i*$Pr_2NH$ (12.5 mL, 72.0 mmol) in dry THF (20 mL) was added slowly to a solution of the compound **9** (9.54 g, 30.0 mmol) in dry THF (100 mL) under an Ar atmosphere. The reaction mixture was stirred for 30 min at room temperature, and then $ClCH_2OMe$ (5.80 g, 5.5 mL, 72.0 mmol) was added by syringe. The resulting mixture was stirred overnight at room temperature. The insoluble ammonium salts were filtered off to give a filtrate. After the solvent was removed in vacuo, column chromatography ($SiO_2$: hexane/$CH_2Cl_2$ = 2:1) was carried out to afford the product **10** (3.50 g, 86%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.69 (s, 6H; $OCH_3$), 5.38 (s, 4H; $OCH_2O$), 7.52–7.54 (d, 2H; Ar-H), 8.08–8.10 ppm (d, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 55.2, 93.8, 103.4, 125.6, 126.1, 129.4, 153.8 ppm; MS (ESI-TRAP): *m*/*z*: 403.89 $[M]^+$.

**Compound 11**: Compound **10** (12.2 g, 30.0 mmol), [$Pd(PPh_3)_4$] (0.60 g, 0.53 mmol), CuI (0.22 g, 1.05 mmol), $PPh_3$ (0.30 g, 1.14 mmol), *i*$Pr_2NH$ (55 mL), and $Et_3N$ (150 mL) were added to a three-necked flask equipped with a condenser and a magnetic stirrer under an inert atmosphere. The mixture was purged with Ar and stirred for 30 min before trimethylsilylacetylene (7.51 g, 76.4 mmol) was added. The reaction mixture was slowly heated to 80°C and stirred for 8 h at this temperature. After cooling the solution to room temperature, the insoluble material was collected by filtration. The solid was extracted with $CH_2Cl_2$ (450 mL). The organic layer was washed with $H_2O$ (2×100 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to afford the crude product. Column chromatography ($SiO_2$: hexane/EtOAc = 2:1) was carried out to provide **11** as a light-yellow solid (12.7 g, 98%). $^1$H NMR (500 MHz, $CD_2Cl_2$, TMS): $\delta$ = 0.40 (s, 18H; $Si(CH_3)_3$), 3.72 (s, 6H; $OCH_3$), 5.40 (s, 4H; $OCH_2O$), 7.59–7.61 (dd, *J* = 6.4, 3.3 Hz, 2H; Ar-H), 8.29–8.31 ppm (dd, *J* = 6.4, 3.3 Hz, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CD_2Cl_2$, TMS): $\delta$ = 0.1, 57.6, 98.7, 99.4, 106.2, 115.1, 125.7, 126.6, 130.8, 151.5 ppm; MS (ESI-TRAP): *m*/*z*: 440.16 $[M]^+$.

**Compound 12**: $K_2CO_3$ (7.62 g, 55.0 mmol) was added to a solution of **11** (12.1 g, 27.4 mmol) in a mixture of $CH_2Cl_2$ (300 mL) and MeOH (300 mL) purged with Ar. The reaction mixture was stirred for 4 h at room temperature. Solvents were removed in vacuo to give a reddish-orange residue, which was dissolved in $CH_2Cl_2$ (350 mL), washed with $H_2O$ (2×200 mL), and dried ($MgSO_4$). The solvent was removed in vacuo to afford an orange solid. Column chromatography ($SiO_2$: hexane/EtOAc = 1:1 to 2:1) was carried out to provide **12** (8.48 g, 96%). $^1$H NMR (500 MHz, $CD_2Cl_2$, TMS): $\delta$ = 3.73 (s, 6H; $OCH_3$), 3.91 (s, 2H; C≡CH), 5.39 (s, 4H; $OCH_2O$), 7.60–7.63 (dd, *J* = 6.3, 3.3 Hz, 2H; Ar-H), 8.32–8.34 ppm (dd, *J* = 6.3, 3.3 Hz, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CD_2Cl_2$, TMS): $\delta$ = 57.7, 77.5, 88.1, 99.6, 114.5, 125.6, 126.7, 130.9, 151.9 ppm; MS (ESI-TRAP): *m*/*z*: 296.07 $[M]^+$.

**Compound 13**: Methyl 4-iodobenzoate (10.6 g, 40.4 mmol), [$Pd(PPh_3)_4$] (0.38 g. 0.37 mmol), CuI (0.14 g, 0.74 mmol), $PPh_3$ (0.20 g, 0.47 mmol), *i*$Pr_2NH$ (45 mL), and $Et_3N$ (100 mL) were added to a three-necked flask equipped with a condenser and a magnetic stirrer under an inert atmosphere. The mixture was purged with Ar followed by stirring for 30 min before **12** (6.00 g, 20.2 mmol) was added. The reaction mixture was slowly heated to 80°C and stirred for 8 h at this temperature. After cooling to room temperature, the insoluble material was removed by filtration and then rinsed with $CH_2Cl_2$ (250 mL). The solution in $CH_2Cl_2$ was combined with the filtrate, and the organic phase was washed with $H_2O$ (2×100 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to afford the product **13** (8.30 g, 73%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.73 (s, 6H; $OCH_3$), 3.96 (s, 6H; $COOCH_3$), 5.46 (s, 4H; $OCH_2O$), 7.61–7.63 (dd, *J* = 6.4, 3.0 Hz, 2H; Ar-H), 7.71–7.73 (d, *J* = 8.4 Hz, 4H; Ar-H), 8.08–8.10 (d, *J* = 8.4 Hz, 4H; Ar-H), 8.59–8.62 ppm (dd, *J* = 6.4, 3.0 Hz, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 52.5, 58.2, 87.4, 99.8, 100.0, 115.6, 126.2, 127.2, 127.9, 129.9, 130.2, 131.1, 131.7, 151.5, 166.7 ppm; MS (ESI-TRAP): *m*/*z*: 564.21 $[M]^+$.

**Compound 14**: Compound **13** (2.50 g, 4.43 mmol) and NaOH (0.71, 17.7 mmol) were dissolved in a mixture of THF (100 mL) and $H_2O$ (100 mL). The reaction and purification procedures were identical to

those described for the preparation of **8**. The product **14** was a yellow solid (2.25 g, 95%). $^1$H NMR (500 MHz, $CD_3SOCD_3$, TMS): $\delta = 3.63$ (s, 6H; $OCH_3$), 5.38 (s, 4H; $OCH_2O$), 7.68–7.70 (dd, $J = 6.2$, 3.2 Hz, 2H; Ar-H), 7.79–7.81 (d, $J = 8.0$ Hz, 4H; Ar-H), 8.03–8.05 (d, $J = 8.0$ Hz, 4H; Ar-H), 8.32–8.35 (dd, $J = 6.2$, 3.2 Hz, 2H; Ar-H), 13.20–13.22 ppm (b, 2H; COOH); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 52.5$, 58.2, 87.4, 99.8, 100.0, 115.6, 126.2, 127.2, 127.9, 129.9, 130.7, 131.1, 131.7, 151.5, 166.7 ppm; MS (ESI-TRAP): $m/z$: 536.09 $[M]^+$.

**Compound 15**:[21] Veratrol (40.0 g, 0.29 mol) was dissolved in a mixture of dry hexane (100 mL) and TMEDA (40 mL). *n*BuLi (1.6 M in hexane, 200 mL, 0.32 mol) was added dropwise at room temperature. The reaction was stirred at room temperature for 28 h and cooled to −78 °C. $ClSiMe_3$ (45 mL) was added slowly and the reaction mixture was allowed to warm to room temperature over 5 h. $H_2O$ was added and the reaction mixture was extracted with hexane. The organic layer was separated and dried ($MgSO_4$). Solvent was removed in vacuo and the residue was purified by flash chromatography ($SiO_2$: hexane/$CH_2Cl_2$ = 10:1) to give the product **15** as a colorless oil (51.5, 85%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 0.38$ (s, 9H; $Si(CH_3)_3$), 3.76 (s, 6H; $OCH_3$), 6.79–6.80 (d, 1H; Ar-H), 6.81–6.82 (d, 1H; Ar-H), 6.84–6.85 ppm (d, 1H; Ar-H).

**Compound 16**: Compound **15** (69.0 g, 0.33 mol) was dissolved in TMEDA (60 mL) and cooled to 0 °C. *n*BuLi in hexane (1.6 M, 250 mL, 0.40 mol) was added dropwise. The reaction mixture was stirred at room temperature for 25 h and then cooled to −78 °C. After $ClSiMe_3$ (60 mL) was added dropwise, the reaction mixture was warmed to room temperature over 5 h. $H_2O$ was added and the reaction mixture was extracted with hexane. The organic layer was separated and dried ($MgSO_4$). Solvent was removed in vacuo and the residue was purified by flash chromatography ($SiO_2$: hexane/$CH_2Cl_2$ = 10:1) to give the product **16** as a colorless oil (82.5 g, 89%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 0.39$ (s, 18H; $Si(CH_3)_3$), 3.77 (s, 6H; $OCH_3$), 6.86 ppm (s, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 2.1$, 56.8, 122.9, 128.1, 152.4 ppm.

**Compound 17**:[22] Compound **16** (19.2 g, 68.1 mmol) was dissolved in $CH_2Cl_2$ (100 mL) and the solution was cooled to 0 °C. A solution of ICl (23.1 g, 0.14 mol) in $CH_2Cl_2$ (100 mL) was added slowly. The reaction mixture was warmed to room temperature, stirred for 30 min, and quenched with an aqueous solution of $Na_2S_2O_3$. The organic layer was separated and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was purified by flash chromatography ($SiO_2$: hexane/$CH_2Cl_2$ = 10:1) to give **17** as a yellowish oil (21.5 g, 81%), which solidified slowly at room temperature. M.p. 46–47 °C. $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 3.87$ (s, 6H; $OCH_3$), 7.24 ppm (s, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 60.8$, 93.0, 135.5, 153.1 ppm.

**Compound 18**:[22,23] Compound **17** (1.80 g, 4.62 mmol) was dissolved in $CH_2Cl_2$ (20 mL) and the solution was cooled to −78 °C. $BBr_3$ (2 mL, 5.30 g, 21.2 mol) was added and the reaction mixture was warmed to room temperature and was stirred for 14 h. The reaction was poured into ice/$H_2O$ and the mixture was extracted with EtOAc, and the organic layer was separated and dried ($Na_2SO_4$). The solvent was removed in vacuo and the residue was purified by flash chromatography ($SiO_2$, $CH_2Cl_2$) to afford **18** as a white solid (1.50 g, 90%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 5.61$ (s, 2H; OH), 7.00 ppm (s, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 83.6$, 131.2, 143.1 ppm.

**Compound 19**: A solution of $i$Pr$_2$NH (12.5 mL, 72.0 mmol) in dry THF (20 mL) was added slowly to a solution of **18** (10.9 g, 30.0 mmol) in dry THF (100 mL) under an Ar atmosphere. The reaction mixture was stirred for 30 min at room temperature and then $ClCH_2OMe$ (5.80 g. 5.5 mL, 72.0 mmol) was added by means of a syringe. The resulting mixture was stirred overnight at room temperature. The insoluble ammonium salts were filtered off to give a light-yellow filtrate. The filtrate was dried under vacuum to obtain a beige powder (13.4 g, 95%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 3.67$ (s, 6H; $OCH_3$), 5.41 (s, 4H; $OCH_2O$), 7.12 ppm (s, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): 55.4, 94.6, 86.1, 132.9, 154.3 ppm; MS (ESI-TRAP): $m/z$: 449.85 $[M]^+$.

**Compound 20**: Compound **19** (6.75 g, 15.0 mmol), $[Pd(PPh_3)_4]$ (0.29 g, 0.39 mmol), CuI (0.11 g, 0.56 mmol)), $PPh_3$ (0.15 g, 0.57 mmol), $i$Pr$_2$NH (28 mL), and $Et_3N$ (80 mL) were added to a three-necked flask equipped with a condenser and a magnetic stirrer under an inert atmosphere. The mixture was purged with Ar followed by stirring for 30 min, and **2** (4.81 g, 30.0 mmol) was then added in one portion. After addition, the reaction mixture was slowly heated to 80 °C and stirred for 8 h at this temperature. After cooling to room temperature, the insoluble material was collected by filtration and washed with $Et_3N$ (30 mL). The solid was extracted with $CH_2Cl_2$ (250 mL), washed twice with $H_2O$ (2×150 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed in vacuo to give the product **20** (6.50 g, 84%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 3.67$ (s, 6H; $OCH_3$), 3.93 (s, 6H; $COOCH_3$), 5.33 (s, 4H; $OCH_2O$), 7.28, (s, 2H; Ar-H), 7.58–7.59 (d, 4H; Ar-H), 8.02–8.04 ppm (d, 4H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 52.3$, 57.8, 57.3, 88.4, 94.4, 99.3, 119.4, 127.5, 128.6, 129.6, 129.8, 131.4, 151.2, 166.4 ppm; MS (ESI-TRAP): $m/z$: 514.14 $[M]^+$.

**Compound 21**: *p*-Toluenesulfonic acid (0.50 g, 2.91 mmol) was added to a solution of **20** (1.70 g, 3.30 mmol) in a mixture of $CH_2Cl_2$ (150 mL) and MeOH (100 mL). The reaction mixture was stirred for 6 d at room temperature to give a grey suspension. The precipitate was collected by filtration, washed with $H_2O$, MeOH, and $CH_2Cl_2$, and dried in air to give compound **21** (1.10 g, 78%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 3.94$ (s, 6H; $COOCH_3$), 5.37 (s, 2H; OH), 7.24, (s, 2H; Ar-H), 7.58–7.60 (d, 4H; Ar-H), 8.02–8.04 ppm (d, 4H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 51.8$, 88.3, 94.6, 119.2, 127.1, 128.2, 129.6, 129.9, 131.6, 132.4, 148.5, 166.4 ppm; MS (ESI-TRAP): $m/z$: 426.13 $[M]^+$.

**Compounds 22 and 23**:[24] A suspension of pyrocatechol (3.20 g, 29.1 mmol), tetraethyleneglycol monotosylate (15.5 g, 44.5 mmol), and $K_2CO_3$ (11.0 g) in MeCN (350 mL) was stirred under reflux in an atmosphere of Ar for 2 d. After cooling to room temperature, the insoluble materials were filtered off to give a light-yellow filtrate. It was dried under reduced pressure to give **22** as a yellow oil, which was treated directly with tosyl chloride (9.25 g, 48.7 mmol) in THF (45 mL) in the presence of an aqueous solution of NaOH (4.11 g, 103 mmol). The resulting mixture was stirred for another day. THF was removed under reduced pressure and the $H_2O$ phase was extracted twice with $CH_2Cl_2$ (2× 150 mL). The organic phase was washed once with a saturated aqueous solution of $NaHCO_3$ (100 mL), twice with $H_2O$ (150 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a yellow residue. It was purified by flash column chromatography ($SiO_2$: EtOAc/MeOH = 98:2) to give the product **23** (10.2 g, 62%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 2.45$ (s, 6H; $CH_3$), 3.59–3.62 (m, 8H; $OCH_2CH_2O$), 3.65–3.69 (m, 8H; $OCH_2CH_2O$), 3.75–3.77 (m, 4H; $OCH_2CH_2O$), 3.93–3.95 (m, 4H; $OCH_2CH_2O$), 4.11–4.14 (m, 4H; $OCH_2CH_2O$), 4.25–4.28 (m, 4H; $OCH_2CH_2O$), 6.90–6.91 (d, 2H; Ar-H), 6.93–6.94 (d, 2H; Ar-H), 7.42–7.44 (d, 4H; Ar-H), 7.71–7.73 ppm (d, 4H; Ar-H).

**DB30C10DE (Scheme 4)**: A three-necked flask was equipped with a magnetic stirrer, a condenser, and a funnel under an inert atmosphere. The flask was charged with $Cs_2CO_3$ (7.50 g, 23.0 mmol) and DMF (200 mL), and the reaction mixture was heated to 100 °C. A solution of compounds **21** (1.70 g, 4.00 mmol) and **23** (3.08 g, 4.00 mmol) in DMF (150 mL) was added slowly to the stirring $Cs_2CO_3$ suspension within 5 h. After addition, the reaction mixture was stirred for 2 d at this temperature. When cooling to room temperature, the reaction mixture was filtered to remove the insoluble material, and the solid was washed with DMF (50 mL). The filtrates were combined together and solvent was removed under reduced pressure to obtain a dark residue. The product was purified by flash column chromatography ($SiO_2$: EtOAc) to give the product DB30C10DE (0.55 g, 16%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 3.65$–4.12 (m, 38H; $OCH_2O$ and $COOCH_3$), 6.82–6.83 (d, 2H; Ar-H), 6.91–6.92 (d, 2H; Ar-H), 7.31 (s, 2H; Ar-H), 7.67–7.69 (d, $J = 8.2$ Hz, 4H; Ar-H), 7.97–7.98 ppm (d, $J = 8.2$ Hz, 4H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 52.2$, 68.5, 69.3, 70.4, 70.7, 70.9, 87.2, 94.9, 113.3, 121.1, 124.8, 127.2, 129.9, 131.7, 148.1, 151.3, 166.5 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{48}H_{53}O_{14}^+$ $[M+H]^+$: 853.3435; found: 853.3431.

**DB30C10DA**: A solution of NaOH (0.45 g, 11.0 mmol) in $H_2O$ (30 mL) was added to a solution of DB30C10DE (0.79 g, 0.93 mmol) in THF (40 mL). The reaction mixture was stirred overnight at room temperature. THF was removed under reduced pressure to give dark-yellow residue, which was acidified by 2 N HCl aqueous (20 mL), forming a yellow

suspension. The yellow precipitate was collected by filtration and washed with $H_2O$. The crude product was recrystallized from $Me_2CO$/MeOH to yield DB30C10DA as a yellow powder (0.70 g, 91%). $^1$H NMR (500 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 3.71–4.22 (m, 32H; $OCH_2O$), 6.84–6.85 (d, 2H; Ar-H), 6.86–6.87 (d, 2H; Ar-H), 7.31 (s, 2H; Ar-H), 7.67–7.68 (d, $J$ = 8.3 Hz, 4H; Ar-H), 7.98–7.99 ppm (d, $J$ = 8.3 Hz, 4H; Ar-H); $^{13}$C NMR (125 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 69.5, 70.3, 70.5, 70.8, 86.7, 95.1, 112.6, 120.9, 124.5, 127.3, 129.9, 132.2, 148.2, 150.8, 168.7 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{46}H_{49}O_{14}^+$ $[M+H]^+$: 825.3122; found: 825.3119.

**Compound 24**: A three-necked flask was equipped with a magnetic stirrer, a condenser, and a funnel under an inert atmosphere. The flask was charged with $Cs_2CO_3$ (7.50 g, 23.0 mmol) and DMF (200 mL), and the reaction mixture was heated to 100°C. A solution of compounds **18** (1.45 g, 4.00 mmol) and **23** (3.08 g, 4.00 mmol) in DMF (150 mL) was added slowly with stirring during 5 h to the $Cs_2CO_3$ suspension. After the addition, the reaction mixture was stirred for a further 2 d at this temperature. On cooling to room temperature, the reaction mixture was filtered to remove the insoluble material, and the solid was washed with DMF (50 mL). The filtrates were combined and the solvent was removed under reduced pressure to obtain a dark residue. The product was purified by flash column chromatography ($SiO_2$: EtOAc/hexane = 3:1) to give the product **24** (1.06 g, 34%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.66–4.07 (m, 32H; $OCH_2O$), 6.91–6.92 (d, 2H; Ar-H), 6.93–6.94 (d, 2H; Ar-H), 7.11 ppm (s, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 68.5, 69.4, 69.5, 70.3, 70.9, 86.2, 120.7, 121.3, 131.6, 150.8, 152.2 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{28}H_{39}I_2O_{10}^+$ $[M+H]^+$: 789.0633; found: 789.0628.

**DB30C10DE (Scheme 5)**: Compound **24** (1.02 g, 1.30 mmol), $[Pd(PPh_3)_4]$ (26.0 mg, 0.02 mmol), CuI (10.0 mg, 0.05 mmol), $PPh_3$ (15.0 mg, 0.06 mmol), $i$Pr$_2$NH (5 mL), $Et_3N$ (15 mL), and THF (15 mL) were added to a three-necked flask equipped with a condenser and a magnetic stirrer under an inert atmosphere. The mixture was purged with Ar while stirring for 30 min, and **2** (0.42 g, 3.20 mmol) was added in one portion. After completing this addition, the reaction mixture was slowly heated to 80°C and stirred for 8 h at this temperature. After cooling to room temperature, the insoluble material was collected by filtration. The solid was extracted with $CH_2Cl_2$ (100 mL) and the organic solution was washed twice with $H_2O$ (2×100 mL) and dried ($MgSO_4$). After removal of the solvent, the pure product was obtained by recrystallization from $CH_2Cl_2$/hexane (0.90 g, 89%).

**Compound 25**: $p$-Toluenesulfonic acid (0.50 g, 2.91 mmol) was added to a solution of **13** (1.86 g, 3.30 mmol) in a mixture of $CH_2Cl_2$ (150 mL) and MeOH (100 mL). The reaction mixture was stirred for 5 d at room temperature to give a yellow suspension. The yellow solid was collected by filtration, washed with $H_2O$ and MeOH, and finally dried in air to give the product **25** (1.30 g, 83%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.89 (s, 6H; $COOCH_3$), 7.50–7.52 (d, 2H; Ar-H), 7.85–7.86 (d, $J$ = 8.4 Hz, 4H; Ar-H), 8.03–8.05 (d, $J$ = 8.4 Hz, 4H; Ar-H), 8.15–8.17 ppm (d, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 52.2, 94.1, 104.8, 124.9, 126.5, 127.2, 130.0, 133.1, 133.7, 148.5, 166.2 ppm; MS (ESI-TRAP): $m/z$: 476.09 $[M]^+$.

**Compounds 26 and 27**:[24] A suspension of 2,3-dihydroxynaphthalene (3.20 g, 20.0 mmol), tetraethyleneglycol monotosylate (15.5 g, 44.0 mmol), and $K_2CO_3$ (11.1 g, 80.0 mmol) in MeCN (350 mL) was stirred and heated under reflux in Ar for 2 d. After cooling to room temperature, the insoluble materials were filtered off to give a light-yellow filtrate. It was dried under reduced pressure to give **26** as a yellow oil, which was treated directly with tosyl chloride (9.25 g, 49.0 mmol) in THF (45 mL) in the presence of an aqueous solution of NaOH (4.12 g, 103 mmol). The resulting mixture was stirred for another day. THF was removed under reduced pressure and the $H_2O$ phase was extracted twice with $CH_2Cl_2$ (2×150 mL). The organic phase was washed once with a saturated aqueous solution of $NaHCO_3$ (100 mL), twice with $H_2O$ (150 mL), and dried ($MgSO_4$). The solvent was removed reduced pressure to give a yellow residue. It was purified by flash column chromatography ($SiO_2$: EtOAc/MeOH = 98:2) to give the product **27** (10.2 g, 62%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 2.43 (s, 6H; $CH_3$), 3.58–3.60 (m, 8H; $OCH_2CH_2O$), 3.66–3.68 (m, 8H; $OCH_2CH_2O$), 3.76–3.78 (m, 4H; $OCH_2CH_2O$), 3.93–3.95 (m, 4H; $OCH_2CH_2O$), 4.12–4.15 (m, 4H; $OCH_2CH_2O$), 4.27–4.29 (m, 4H; $OCH_2CH_2O$), 7.16 (s, 2H; Ar-H), 7.31–7.34 (m, 6H; Ar-H), 7.65–7.67 (d, 2H; Ar-H), 7.78–7.79 ppm (d, 4H; Ar-H).

**DN30C10DE (Scheme 6)**: A three-necked flask was equipped with a magnetic stirrer, a condenser, and a funnel under an inert atmosphere. The flask was charged with $Cs_2CO_3$ (2.74 g, 8.00 mmol) and DMF (150 mL), and the reaction mixture was heated to 100°C. A solution of compounds **25** (1.00 g, 2.10 mmol) and **27** (1.72 g, 2.10 mmol) in DMF (100 mL) was added slowly with stirring to the $Cs_2CO_3$ suspension within 5 h. After the addition, the reaction mixture was stirred for 2 d at this temperature. On cooling to room temperature, the reaction mixture was filtered to remove the insoluble material and the solid was washed with DMF (50 mL). The filtrates were combined and the solvent was removed under reduced pressure to give a dark residue. The product was purified by flash column chromatography ($SiO_2$: EtOAc) to give the product DN30C10DE (0.30 g, 15%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.41–4.18 (m, 38H; $OCH_2O$ and $COOCH_3$), 7.26–7.28 (m, 4H; Ar-H), 7.66–7.70 (m, 4H; Ar-H), 7.82–7.83 (d, 4H; Ar-H), 8.03–8.04 (d, 4H; Ar-H), 8.32–8.34 ppm (d, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 52.3, 69.1, 69.6, 70.4, 70.9, 94.3, 101.4, 107.2, 124.5, 127.1, 129.8, 130.7, 132.6, 135.1, 150.0, 154.4, 166.1 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{56}H_{57}O_{14}^+$ $[M+H]^+$: 953.3748; found: 953.3750.

**DN30C10DA**: A solution of NaOH (0.55 g, 13.8 mmol) in $H_2O$ (40 mL) was added to a solution of DN30C10DE (0.92 g, 0.97 mmol) in THF (40 mL). The reaction mixture was stirred overnight at room temperature. THF was removed under reduced pressure to give a dark-yellow residue, which was acidified by a 2N aqueous solution of HCl (20 mL) to form a yellow suspension. The yellow precipitate was collected by filtration and washed with $H_2O$. The crude product was recrystallized from $Me_2CO$/MeOH to yield DN30C10DA as a yellow powder (0.75 g, 84%). $^1$H NMR (500 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 3.53–4.20 (m, 32H; $OCH_2O$), 7.25–7.28 (m, 4H; Ar-H), 7.69–7.71 (m, 4H; Ar-H), 7.81–7.83 (d, 4H; Ar-H), 8.04–8.05 (d, 4H; Ar-H), 8.31–8.33 ppm (d, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 68.9, 69.7, 70.5, 70.9, 71.2, 94.1, 101.4, 106.7, 124.9, 127.1, 128.3, 130.5, 132.7, 135.1, 150.5, 154.3, 170.2 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{54}H_{53}O_{14}^+$ $[M+H]^+$: 925.3435; found: 925.3431.

**Compound 28**: A three-necked flask was equipped with a magnetic stirrer, a condenser, and a funnel under an inert atmosphere. The flask was charged with $Cs_2CO_3$ (8.20 g, 25.0 mmol) and DMF (250 mL), and the reaction mixture was heated up to 100°C. A solution of compounds **9** (1.60 g, 5.00 mmol) and **27** (4.10 g, 5.00 mmol) in DMF (300 mL) was added slowly to the stirred $Cs_2CO_3$ suspension during 5 h. After the addition, the reaction mixture was stirred for 2 d at this temperature. After cooling to room temperature, the reaction mixture was filtered to remove the insoluble material, and the solid was washed with DMF (50 mL). The filtrates were combined and the solvent was removed under reduced pressure to obtain a dark residue, which was purified by flash column chromatography ($SiO_2$: hexane/EtOAc = 1:3) to give the product **28** (1.56 g, 39%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.45–4.20 (m, 38H; $OCH_2O$ and $COOCH_3$), 7.28–7.30 (m, 4H; Ar-H), 7.68–7.72 (m, 4H; Ar-H), 8.33–8.35 ppm (d, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 69.2, 69.7, 70.5, 71.1, 104.3, 107.1, 124.8, 126.2, 126.8, 129.7, 150.4, 154.6 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{36}H_{43}Br_2O_{10}^+$ $[M+H]^+$: 793.1223; found: 793.1218.

**DN30C10DE (Scheme 7)**: Compound **28** (1.27 g, 1.60 mmol), $[Pd(PPh_3)_4]$ (30.0 mg, 0.03 mmol), CuI (10 mg, 0.05 mmol), $PPh_3$ (15.0 mg, 0.06 ppm), $i$Pr$_2$NH (5 mL), $Et_3N$ (15 mL), and DMF (15 mL) were added to a three-necked flask equipped with a condenser and a magnetic stirrer under an inert atmosphere. The mixture was purged with Ar while stirring for 30 min, and **2** (0.52 g, 3.20 mmol) was added in one portion. After the addition, the reaction mixture was slowly heated to 100°C and stirred for 8 h at this temperature. After cooling to room temperature, the insoluble material was collected by filtration. The solid was extracted with $CH_2Cl_2$ (100 mL), and the organic layer was washed twice with $H_2O$ (2×100 mL)

and dried ($MgSO_4$). After removal of solvent, the product was recrystallized from $CH_2Cl_2$/hexane to give DN30C10DE (1.10 g, 72%).

**Compound 29**: A solution of 2,5-dibromohydroquinone (9.38 g, 35.0 mmol) and $K_2CO_3$ (19.3 g, 140 mmol) in MeCN (400 mL) was heated under reflux in an inert atmosphere for 30 min. A solution of tetraethyleneglycol monotosylate (26.9 g, 77.0 mmol) in MeCN (40 mL) was added dropwise to the mixture over 30 min. Stirring and heating were continued for 3 d. The reaction mixture was then filtered and the solvent was removed in vacuo. The residue was purified by column chromatography ($SiO_2$: $CH_2Cl_2$/MeOH = 9:1) to yield compound **29** as a white solid (13.7 g, 63%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 2.72–2.73 (b, 2H; OH), 3.57–4.13 (m, 32H; $OCH_2O$), 7.14 ppm (s, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 61.9, 69.8, 70.3, 70.5, 70.8, 71.3, 72.7, 111.6, 119.3, 150.4 ppm; HRMS (ESI-TOF): *m*/*z* calcd for $C_{22}H_{37}Br_2O_{10}^+$ $[M+H]^+$: 619.0748; found: 619.0753.

**Compounds 30 and 31**: Compound **29** (3.10 g, 5.00 mmol), **2** (1.76 g, 11.0 mmol), $[Pd(PPh_3)_4]$ (289 mg, 0.25 mmol), and CuI (47.5 mg, 0.25 mmol) were added to a mixture of $Et_3N$ (50 mL) and DMF (50 mL). The mixture was stirred at 90°C for 3 d before the solvent was removed in vacuo. The residue was then dissolved in $CH_2Cl_2$ (50 mL) before $Et_3N$ (7.0 mL, 50 mmol), 4-dimethylaminopyridine (122 mg, 1.00 mmol), and a solution of *p*-toluenesylfonyl chloride (2.29 g, 12.0 mmol) in $CH_2Cl_2$ (5 mL) were added into the solution. The solution was stirred for 3 h before being washed with 1 M aqueous HCl (100 mL) and $H_2O$ (2× 100 mL), and then dried ($MgSO_4$). The solvent was then removed in vacuo and the residue was purified by column chromatography ($SiO_2$: $CH_2Cl_2$/EtOAc = 2:1) to yield **31** as a yellow solid (2.72 g, 50%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 2.42 (s, 6H; Ts-$CH_3$), 3.56–4.22 (m, 38H; $OCH_2O$ and $COOCH_3$), 7.06 (s, 2H; Ar-H), 7.30–7.31 (d, *J* = 8.2 Hz, 4H; Ar-H), 7.58–7.59 (d, *J* = 8.3 Hz, 4H; Ar-H), 7.78–7.79 (d, *J* = 8.2 Hz, 4H; Ar-H), 8.01–8.03 ppm (d, *J* = 8.4 Hz, 4H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 20.6, 51.3, 67.6, 68.2, 68.5, 68.7, 69.5, 69.7, 70.1, 87.7, 93.5, 113.0, 116.2, 126.9, 128.5, 128.6, 128.8, 130.4, 131.9, 143.8, 152.7, 165.5 ppm; HRMS (ESI-TOF): *m*/*z* calcd for $C_{56}H_{63}O_{18}S_2^+$ $[M+H]^+$: 1087.3450; found: 1087.3477.

**NPP36C10DE**: A solution of **31** (820 mg, 0.76 mmol), 1,5-dihydroxynaphthalene (121 mg, 0.76 mmol), and $Cs_2CO_3$ (984 mg, 3.02 mmol) were dissolved in DMF (80 mL). The solution was stirred and heated under reflux in an inert atmosphere for 3 d. The reaction mixture was filtered and the solvent was removed. The resulting residue was purified by column chromatography ($SiO_2$: $Et_2O/CH_2Cl_2$ = 1:1) to yield NPP36C10DE as a bright-yellow solid (136 mg, 20%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.69–4.18 (m, 38H; $OCH_2O$ and $COOCH_3$), 6.66–6.67 (d, *J* = 8.4 Hz, 2H; Ar-H), 6.84 (s, 2H; Ar-H), 7.22–7.24 (t, *J* = 8.4 Hz, 2H; Ar-H), 7.56–7.57 (d, *J* = 8.4 Hz, 4H; Ar-H), 7.78–7.79 (d, *J* = 8.4 Hz, 2H; Ar-H), 8.00–8.02 ppm (d, *J* = 8.4 Hz, 4H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 52.3, 67.8, 68.2, 69.6, 69.7, 70.8, 70.9, 71.0, 88.9, 94.4, 105.5, 113.7, 114.5, 116.6, 125.0, 126.6, 128.0, 129.4, 129.5, 131.5, 153.5, 154.2, 166.6 ppm; HRMS (ESI-TOF): *m*/*z* calcd for $C_{52}H_{55}O_{14}^+$ $[M+H]^+$: 903.3586; found: 903.3604.

**NPP36C10DA**: A solution of NPP36C10DE (130 mg, 0.14 mmol) and KOH (78.4 mg, 1.40 mmol) were dissolved in a mixture of MeOH (2.5 mL) and $CH_2Cl_2$ (2.5 mL). The solution was stirred overnight. The reaction mixture was then filtered and solvent was removed. The residue was purified by column chromatography ($SiO_2$: $CH_2Cl_2$/MeOH/AcOH = 9:1:0.01) to yield NPP36C10DA as a bright-yellow solid (121 mg, 96%). $^1$H NMR (500 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 3.53–4.10 (m, 32H; $OCH_2O$), 6.71–6.73 (d, *J* = 8.3 Hz, 2H; Ar-H), 7.09 (s, 2H; Ar-H), 7.21–7.23 (t, *J* = 8.3 Hz, 2H; Ar-H), 7.59–7.60 (d, *J* = 8.4 Hz, 4H; Ar-H), 7.61–7.62 (d, *J* = 8.3 Hz, 2H; Ar-H), 7.93–7.94 (d, *J* = 8.4 Hz, 4H; Ar-H), 12.8–12.9 ppm (b, 2H; COOH); $^{13}$C NMR (125 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 68.1, 69.2, 69.3, 70.3, 70.4, 70.5, 70.6, 89.2, 94.7, 106.1, 113.4, 114.1, 116.8, 125.5, 126.3, 127.2, 129.9, 130.9, 131.7, 153.5, 154.1, 172.3 ppm; HRMS (ESI-TOF): *m*/*z* calcd for $C_{50}H_{51}O_{14}^+$ $[M+H]^+$: 875.3273; found: 875.3250.

**Compounds 32 and 33**:[25] A suspension of hydroquinone (3.20 g, 29.1 mmol), tetraethyleneglycol monotosylate (15.5 g, 44.5 mmol), and $K_2CO_3$ (11.0 g) in MeCN (350 mL) was stirred under reflux in an atmosphere of Ar for 2 d. After cooling to room temperature, the insoluble materials were filtered off to give a light-yellow filtrate. It was dried under reduced pressure to give **32** as a yellow oil, which was treated directly with tosyl chloride (9.25 g, 48.7 mmol) in THF (45 mL) in the presence of an aqueous solution of NaOH (4.11 g, 103 mmol). The resulting mixture was stirred for another day. THF was removed under reduced pressure, and the $H_2O$ phase was extracted twice with $CH_2Cl_2$ (2× 150 mL). The organic phase was washed once with a saturated aqueous solution of $NaHCO_3$ (100 mL), twice with $H_2O$ (150 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a yellow residue. It was purified by flash column chromatography ($SiO_2$: EtOAc/MeOH = 98:2) to give the product **33** (12.3 g, 55%). $^1$H NMR (500 MHz, $CD_2Cl_2$, TMS): $\delta$ = 2.48 (s, 6H; $CH_3$), 3.58–3.87 (m, 24H; $OCH_2CH_2O$), 4.15–4.21 (m, 8H; $OCH_2CH_2O$), 6.79 (s, 4H; Ar-H), 7.40–7.41 (d, 4H; Ar-H), 7.81–7.82 ppm (d, 4H; Ar-H).

**Compound 34**: Compound **33** (2.79 g, 3.62 mmol) and 2,5-dibromohydroquinone (0.97 g, 3.63 mmol) were dissolved in DMF (180 mL) in a flame-dried, three-necked, round-bottomed flask. After $Cs_2CO_3$ (2.37 g, 7.26 mmol) was added to the solution, the mixture was stirred under Ar at 90°C for 3 d. The solvent was removed in vacuo and the residue was then dissolved in $CH_2Cl_2$ (100 mL) before being washed with brine (3× 50 mL). The organic phase was dried ($Na_2SO_4$) and the solvent was then removed in vacuo. Column chromatography ($SiO_2$: $Et_2O/CH_2Cl_2$ = 2:1) was carried out to provide the product **34** as a white solid (0.65 g, 26%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.68–4.05 (m, 32H; $OCH_2O$), 6.74 (s, 4H; Ar-H), 7.07 ppm (s, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 68.2, 69.6, 69.8, 70.3, 70.8, 70.9, 71.0, 71.1, 111.4, 115.6, 119.1, 150.3, 153.1 ppm; HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{39}Br_2O_{10}^+$ $[M+H]^+$: 693.0904; found: 693.0902.

**BPP34C10DE (Scheme 9)**: Compound **34** (0.10 g, 0.14 mmol) and **2** (0.05 g, 0.32 mmol) were dissolved in a mixture of DMF (3 mL) and $iPr_2NH$ (1 mL). Under Ar protection, $[PdCl_2(PPh_3)_2]$ (0.01 g, 0.014 mmol) and CuI (0.003 g, 0.014 mmol) were added to the solution. The mixture was stirred under Ar at 90°C for 48 h before the solvent was removed in vacuo. The residue was then dissolved in $CH_2Cl_2$ (5 mL) before being washed with $H_2O$ (2×3 mL) and brine (3 mL). The organic phase was dried ($Na_2SO_4$) and the solvent was then removed in vacuo. Column chromatography ($SiO_2$: $Et_2O/CH_2Cl_2$ = 2:1) was carried out to provide BPP34C10DE as a yellow fluorescent solid (0.10 g, 84%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.64–4.13 (m, 38H; $OCH_2O$ and $COOCH_3$), 6.68 (s, 4H; Ar-H), 7.00 (s, 2H; Ar-H), 7.60–7.61 (d, *J* = 8.2 Hz, 4H; Ar-H), 8.01–8.02 ppm (d, *J* = 8.2 Hz, 4H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 52.1, 68.0, 69.5, 69.6, 70.6, 70.7, 70.9, 71.0, 88.7, 94.5, 115.3, 117.0, 127.9, 129.4, 131.4, 152.9, 153.7, 166.4 ppm; HRMS (ESI-TOF): *m*/*z* calcd for $C_{48}H_{53}O_{14}^+$ $[M+H]^+$: 853.3435; found: 853.3433.

**BPP34C10DA**: BPP34C10DE (0.20 g, 0.24 mmol) and KOH (0.05 mg, 0.94 mmol) were dissolved in a mixture of MeOH (10 mL), $CH_2Cl_2$ (10 mL), and THF (10 mL). The following reaction and purification procedures were identical to those described for the preparation of NPP36C10DA. The product BPP34C10DA was a yellow solid (0.18 g, 94%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.63–4.13 (m, 32H; $OCH_2O$), 6.67 (s, 4H; Ar-H), 6.99 (s, 2H; Ar-H), 7.57–7.58 (d, *J* = 8.3 Hz, 4H; Ar-H), 8.04–8.05 (d, *J* = 8.3 Hz, 4H; Ar-H), 13.23–13.24 ppm (b, 2H; COOH); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 68.1, 69.6, 69.7, 69.8, 70.7, 70.8, 71.0, 71.1, 89.2, 94.6, 115.5, 117.2, 128.7, 128.8, 130.1, 131.6, 153.0, 153.9, 170.2 ppm; HRMS (ESI-TOF): *m*/*z* calcd for $C_{46}H_{49}O_{14}^+$ $[M+H]^+$: 825.3122; found: 825.3115.

**Compound 35**: A three-necked flask was equipped with a magnetic stirrer, a condenser, and a funnel under an inert atmosphere. The flask was charged with $Cs_2CO_3$ (13.0 g, 40.0 mmol) and DMF (450 mL), and the reaction mixture was heated up to 100°C. A solution of 2,5-diiodohydroquinone (2.90 g, 8.00 mmol) and **33** (6.17 g, 8.00 mmol) in DMF (300 mL) was added slowly to the stirred $Cs_2CO_3$ suspension within 5 h. After the addition, the reaction mixture was stirred for 2 d at this temperature. On cooling the solution to room temperature, the reaction mixture was filtered to remove the insoluble material, and the solid was washed with DMF (50 mL). The filtrates were combined and the solvent was removed

under reduced pressure to obtain a dark residue. The product was purified by flash column chromatography ($SiO_2$: hexane/EtOAc = 1:3) to give the compound **35** (3.04 g, 48%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.69–4.04 (m, 32H; $OCH_2O$), 6.75 (s, 4H; Ar-H), 7.10 ppm (s, 2H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 68.1, 69.6, 70.0, 70.5, 70.7, 70.9, 71.1, 71.2, 86.1, 115.4, 120.3, 150.5, 152.8 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{28}H_{39}I_2O_{10}^+$ $[M+H]^+$: 789.0633; found: 789.0630.

**BPP34C10DE (Scheme 10)**: Compound **35** (2.85 g, 3.60 mmol), $[Pd(PPh_3)_4]$ (80.0 mg, 0.07 mmol), CuI (30.0 mg, 0.16 mmol), $PPh_3$ (45.0 mg, 0.17 mmol), $i$Pr$_2$NH (7 mL), and $Et_3N$ (25 mL) were added to a three-necked flask, equipped with a condenser and a magnetic stirrer under an inert atmosphere. The mixture was purged with Ar and stirred for 30 min, while compound **2** (1.38 g, 8.60 mmol) was added in one portion. After the addition, the reaction mixture was slowly heated to 80°C and stirred for 8 h at this temperature. After cooling to room temperature, the solvent was removed under reduced pressure to yield a yellowish-orange residue, which was extracted with $CH_2Cl_2$ (200 mL) and washed twice with $H_2O$ (2×150 mL). The organic layer was dried ($MgSO_4$). After removal of solvent, the product was purified by flash column chromatography ($SiO_2$: hexane/EtOAc = 1:3) to give BPP34C10DE (2.63 g, 87%).

**BPP34C10DE (Scheme 11)**: A solution of **31** (1.09 g, 1.00 mmol), hydroquinone (0.11 g, 1.00 mmol), and $Cs_2CO_3$ (1.30 g, 4.00 mmol) in DMF (100 mL) was stirred and heated under reflux in an inert atmosphere for 5 d. The reaction mixture was filtered and the filtrate was removed. The residue was purified by column chromatography ($SiO_2$: $Et_2O/CH_2Cl_2$ = 1:1) to yield BPP34C10DE as a yellow solid (0.20 g, 24%).

**Compound 36**:[26] PPTS (100 mg, 0.40 mmol) was added to an Ar-blanketed solution of 2,5-dibromohydroquinone (15.0 g, 56.0 mmol) in 3,4-dihydro-2*H*-pyran (DHP; 20 mL). A mildly exothermic reaction ensued and the suspension obtained was allowed to stir at room temperature for 12 h. Excess DHP was removed under vacuum and the residue was quenched with a saturated aqueous solution of $NaHCO_3$ (150 mL), extracted into $CH_2Cl_2$ (2×500 mL), washed with $H_2O$ (2×150 mL), and dried ($MgSO_4$). The mixture was filtered through a pad of silica and the solvent was removed to yield a cream-white solid. Recrystallization from hexane/$CH_2Cl_2$ afforded the compound **36** as an off-white solid (21.5 g, 88%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 1.64–1.73 (m, 8H; $CH_2$), 1.86–2.06 (m, 4H; $CH_2$), 3.60–3.64 (m, 2H; $OCH_2$), 3.91 (s, 2H; $OCH_2$), 5.38–5.39 (t, 2H; OCHO), 7.32 ppm (s, 2H; Ar-H).

**Compound 37**:[26a] Ar was bubbled through a solution of $i$Pr$_2$NH (38 mL) and $Et_3N$ (105 mL) for 30 min. Compound **36** (9.16 g, 21.0 mmol) followed by CuI (0.15 g, 0.78 mmol), $PPh_3$ (0.20 g, 0.75 mmol), and $[Pd(PPh_3)_4]$ (0.40 g, 0.35 mmol) were added and allowed to stir at room temperature for 30 min. Trimethylsilylacetylene (7.5 mL, 54.0 mmol) was added and the mixture was heated at 80°C for 6 h. The precipitates were collected by filtration, and the solid was extracted with $CH_2Cl_2$ and washed twice with $H_2O$ (2×250 mL). The organic layer was dried ($MgSO_4$). After removal of solvent, the product **37** was obtained (8.20 g, 83%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 0.22 (s, 18H; $Si(CH_3)_3$), 1.64–2.30 (m, 12H; $CH_2$), 3.60–3.63 (m, 2H; $OCH_2$), 3.95 (s, 2H; $OCH_2$), 5.46–5.47 (t, 2H; OCHO), 7.18 ppm (s, 2H; Ar-H).

**Compound 38**:[26a] Compound **37** (12.2 g, 26.0 mmol) was dissolved in an Ar-blanketed mixture of $CH_2Cl_2$ (250 mL) and MeOH (100 mL), and KOH (4.20 g, 76.0 mmol) was then added. The mixture was heated under gentle reflux for 10 min and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography ($SiO_2$: hexane/$CH_2Cl_2$ = 7:3) to yield the product **38** as a pale-yellow solid (8.2 g, 87%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 1.60–2.05 (m, 12H; $CH_2$), 3.36 (s, 2H; CCH), 3.58–3.64 (m, 2H; $OCH_2$), 3.96 (s, 2H; $OCH_2$), 5.43–5.44 (t, 2H; OCHO), 7.23 ppm (s, 2H; Ar-H).

**Compound 39**: Methyl 4-iodobenzoate (8.83 g, 33.7 mmol), $[Pd(PPh_3)_4]$ (0.29 g. 0.28 mmol), CuI (0.10 g, 0.52 mmol), $PPh_3$ (0.15 g, 0.35 mmol), $i$Pr$_2$NH (28 mL), and $Et_3N$ (75 mL) were added to a three-necked flask equipped with a condenser and a magnetic stirrer under an inert atmosphere. The mixture was purged with Ar and stirred for 30 min, and compound **38** (5.00 g, 15.3 mmol) was added in one portion. After the addition, the reaction mixture was slowly heated to 80°C and stirred for 8 h at this temperature. After cooling to room temperature, the insoluble material was collected by filtration, and then the solid was washed with $H_2O$ (350 mL) and extracted with $CH_2Cl_2$ (300 mL). The organic layer was washed twice with $H_2O$ (2×150 mL) and dried ($MgSO_4$). After removal of the solvent, the compound **39** was obtained (7.55 g, 83%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 1.59–2.03 (m, 12H; $CH_2$), 3.57–3.62 (m, 2H; $OCH_2$), 3.94 (s, 6H; $COOCH_3$), 3.97 (s, 2H; $OCH_2$), 5.43–5.44 (t, 2H; OCHO), 7.06 (s, 2H; Ar-H), 7.62–7.64 (d, $J$ = 8.4 Hz, 4H; Ar-H), 8.02–8.04 ppm (d, $J$ = 8.4 Hz, 4H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 20.9, 26.1, 30.8, 52.0, 63.8, 87.3, 95.2, 103.6, 111.9, 118.5, 127.6, 129.3, 129.7, 131.8, 152.0, 166.1 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{36}H_{35}O_8^+$ $[M+H]^+$: 595.2332; found: 595.2329.

**Compound 40 (shown in Scheme 12)**: $p$-Toluenesulfonic acid (1.42 g, 8.27 mmol) was added to a solution of **39** (4.92 g, 8.27 mmol) in a mixture of $CH_2Cl_2$ (150 mL) and MeOH (100 mL). The reaction mixture was stirred overnight at room temperature to give a yellow suspension. The yellow precipitate was collected by filtration, washed by MeOH, and dried to afford the compound **40** (3.38 g, 86%). $^1$H NMR (500 MHz, $CDCl_3$, TMS): $\delta$ = 3.92 (s, 6H; $COOCH_3$), 5.38 (s, 2H; OH), 7.09 (s, 2H; Ar-H), 7.63–7.64 (d, $J$ = 8.4 Hz, 4H; Ar-H), 8.03–8.05 ppm (d, $J$ = 8.4 Hz, 4H; Ar-H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS): $\delta$ = 52.1, 85.8, 95.7, 115.2, 121.1, 127.3, 129.4, 129.9, 132.0, 152.4, 165.8 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{26}H_{19}O_6^+$ $[M+H]^+$: 427.1182; found: 427.1178.

**BPP34C10DE (Scheme 12)**: A three-necked flask was equipped with a magnetic stirrer, a condenser, and a funnel under an inert atmosphere. The flask was charged with $Cs_2CO_3$ (3.91 g, 12.0 mmol) and DMF (250 mL), and the reaction mixture was heated to 100°C. A solution of compounds **40** (1.28 g, 3.00 mmol) and **33** (2.31 g, 3.00 mmol) in DMF (200 mL) was added slowly to the stirred $Cs_2CO_3$ suspension within 5 h. After the addition, the reaction mixture was stirred for 2 d at this temperature. On cooling to room temperature, the reaction mixture was filtered to remove the insoluble material, and the solid was washed with DMF (50 mL). The filtrates were combined and the solvent was removed under reduced pressure to give a dark residue. The product was purified by flash column chromatography ($SiO_2$: hexane/EtOAc = 1:3) to give BPP34C10DE (0.26 g, 10%).

**Compound 40 (shown in Scheme 13)**: A solution of $BBr_3$ (1.20 g, 4.80 mmol) in $CH_2Cl_2$ (45 mL) was added dropwise to a solution of **7** (0.91 g, 2.00 mmol) in $CH_2Cl_2$ (20 mL) at −78°C under Ar. The reaction mixture was warmed to room temperature and stirred overnight. When the reaction mixture was poured into ice/$H_2O$ (150 mL), it yielded a yellow precipitate. The yellow solid was collected by filtration, washed with $H_2O$ and MeOH, and dried in air to give **40** as a yellow powder. The $^1$H NMR spectrum shows that this yellow powder is a mixture and the target compound cannot be isolated under the current experimental conditions.

**$H_2$NPP36C10DC-CAT·4 $PF_6$**: NPP36C10DA (52.5 mg, 0.06 mmol), 1,1′-(1,4-phenylenebis(methylene))di-4,4′-bipyridin-1-ium bis(hexafluorophosphate) (84.8 mg, 0.12 mmol), and 1,4-bis(bromomethyl)benzene (15.8 mg, 0.06 mmol) were dissolved in DMF (2 mL). The mixture was stirred at room temperature for 7 d and the solvent was then removed in vacuo. Column chromatography ($SiO_2$: MeOH/$NH_4Cl$ (2 M)/$MeNO_2$ = 7:2:1) was then performed to give a red product. $H_2O$ was then added to dissolve the residue. A saturated aqueous solution of $NH_4PF_6$ was added to the solution until the red precipitate stopped forming. The precipitate was collected by filtration, washed with $H_2O$, EtOH, and $Et_2O$, and then dried in air to provide $H_2$NPP36C10DC-CAT·4 $PF_6$ as a dark-red solid (53.4 mg, 45%). $^1$H NMR (500 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 2.17–2.18 (d, 2H; DNP-H), 3.17–4.18 (m, 32H; $OCH_2O$), 5.65 (s, 8H; $N^+$-$CH_2$), 6.07–6.09 (m, 2H; DNP-H), 6.18–6.20 (d, 2H; DNP-H), 6.44 (s, 2H; Ar-H), 7.17–7.24 (m, 4H; Ar-H), 7.51 (s, 8H; $C_6H_4$), 7.88–7.98 (m, 4H; Ar-H), 8.37–8.41 (m, 8H; β-H), 9.15–9.16 (b, 8H; α-H), 10.56–10.57 ppm (b, 2H; COOH); HRMS (ESI-TOF): $m/z$ calcd for $[M\cdot 2PF_6]^{2+}$: 842.2557; found: 842.2549.

**BPP34C10DE-CAT·4 $PF_6$**: BPP34C10DE (51.2 mg, 0.06 mmol), 1,1′-(1,4-phenylenebis(methylene)) di-4,4′-bipyridin-1-ium (42.4 mg, 0.06 mmol), and 1,4-bis(bromomethyl)benzene (15.8 mg, 0.06 mmol) were dissolved in DMF (2 mL). The following reaction and purification procedures were

identical to those described for the preparation of NPP36C10DA-CAT·4 $PF_6$. The product BPP34C10DE-CAT·4 $PF_6$ was obtained as a dark-red solid (0.69 g, 55 %). $^1$H NMR (500 MHz, $CD_3CN$, TMS): $\delta$ = 3.34–4.00 (m, 42 H; $OCH_2O$, $COOCH_3$, and Ar-H), 5.66 (s, 8 H; $N^+$-$CH_2$), 6.44 (s, 2 H; Ar-H), 7.69–7.70 (d, $J$ = 8.3 Hz, 4 H; Ar-H), 7.71–7.72 (d, $J$ = 6.6 Hz, 8 H; β-H), 7.80 (s, 8 H; $C_6H_4$), 8.14–8.15 (d, $J$ = 8.3 Hz, 4 H; Ar-H), 8.92–8.93 ppm (d, $J$ = 6.6 Hz, 8 H; α-H); $^{13}$C NMR (125 MHz, $CD_3CN$, TMS): $\delta$ = 52.1, 63.8, 66.0, 68.8, 69.6, 69.8, 70.6, 70.8, 71.2, 87.4, 95.5, 112.9, 116.0, 125.3, 130.0, 130.6, 131.9, 137.2, 144.7, 145.7, 149.8, 151.2, 151.5, 164.5 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{84}H_{84}F_{18}N_4O_{14}P_3^+$ [$M$·3 $PF_6$]$^+$: 1807.49; found: 1807.40.

**$H_2$BPP34C10DC-CAT·4 $PF_6$**: BPP34C10DA (49.5 mg, 0.06 mmol), 1,1′-(1,4-phenylenebis(methylene)) di-4,4′-bipyridin-1-ium bis(hexafluorophosphate) (84.8 mg, 0.12 mmol), and 1,4-bis(bromomethyl)benzene (15.8 mg, 0.06 mmol) were dissolved in DMF (2 mL). The following reaction and purification procedures were identical to those described for the preparation of $H_2$NPP36C10DC-CAT·4 $PF_6$. The product $H_2$BPP34C10DC-CAT·4 $PF_6$ was obtained as a dark-red solid (0.64 g, 55 %). $^1$H NMR (500 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 3.37–3.87 (m, 36 H; $OCH_2O$ and Ar-H), 5.67 (s, 8 H; $N^+$-$CH_2$), 6.41 (s, 2 H; Ar-H), 7.55–7.56 (d, $J$ = 8.3 Hz, 4 H; Ar-H), 7.85 (s, 8 H; $C_6H_4$), 8.00–8.01 (d, $J$ = 8.3 Hz, 4 H; Ar-H), 8.07–8.09 (b, 8 H; β-H), 9.20–9.21 (b, 8 H; α-H), 11.45–11.46 ppm (b, 2 H; COOH); $^{13}$C NMR (125 MHz, $CD_3SOCD_3$, TMS): $\delta$ = 63.8, 66.0, 68.8, 69.6, 69.7, 69.9, 70.0, 70.5, 70.8, 87.6, 95.5, 112.4, 116.0, 125.3, 130.0, 130.7, 131.5, 137.1, 144.7, 145.5, 151.3, 152.4, 167.3, 169.7 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{82}H_{80}F_{18}N_4O_{14}P_3^+$ [$M$·3 $PF_6$]$^+$: 1779.46; found: 1779.41.

**$^{15}$N-Labeled DMBP·2 $PF_6$**: Under an inert atmosphere, $CH_3I$ (4.67 g, 32.9 mmol) was added dropwise to $^{15}$N-labeled $C_6H_5N$ (2.00 g, 25.3 mmol). The mixture was stirred at 50 °C for 12 h before MeOH (0.5 mL) was added. The mixture was stirred for another 10 min before the solvents were removed in vacuo. The resulting white solid was dissolved in a mixture of EtOH (8 mL), MeOH (8 mL), and $H_2O$ (8 mL) together with NaCN (3.05 g, 63.2 mmol) and NaOH (1.21 g, 30.3 mmol). The solution was heated to reflux for 30 min, and a dark-blue solution resulted. After the solution had cooled to room temperature, $ZnSO_4$·7 $H_2O$ (10.2 g, 35.4 mmol) was added and a precipitate started to form. The mixture was kept at room temperature without stirring for 1 h before the precipitate was removed by filtration. The pH of the filtrate was then adjusted to 5 with $H_2SO_4$. $O_2$ was then bubbled into the solution for 12 h while the temperature of the solution was maintained below 50 °C. The color of the solution turned from violet to tan. A saturated aqueous solution of $NH_4PF_6$ was then added until no more precipitate formed. The precipitate was collected by filtration, washed with $H_2O$, EtOH, and $Et_2O$, and then dried in air. The product was a white solid (3.90 g, 70 %). $^1$H NMR (500 MHz, $CD_3COCD_3$, TMS): $\delta$ = 4.76 (s, 6 H; $CH_3$), 8.86–8.87 (d, $J$ = 6.5 Hz, 4 H; β-H), 9.39–9.40 ppm (d, $J$ = 6.5 Hz, 4 H; α-H); $^{13}$C NMR (125 MHz, $CD_3COCD_3$, TMS): $\delta$ = 52.2, 126.7, 146.5, 151.5 ppm; HRMS (ESI-TOF): $m/z$ calcd for $C_{12}H_{14}F_6N_2P^+$ [$M$·$PF_6$]$^+$: 331.079; found: 331.082.

**DMBP·2 $PF_6$⊂BPP34C10DA**: BPP34C10DA (9.01 mg, 0.01 mmol) and DMBP·2 $PF_6$ (4.76 mg, 0.01 mmol) were dissolved in $Me_2CO$ (5 mL) in a 20 mL vial. $n$-Pentane was added to the solution until some precipitation was observed. The mixture was filtered to obtain a saturated solution. The solution was left at room temperature for 3 d, and the red, block-shape crystals were observed on the vial wall and then collected for the X-ray crystallographic analyses.

**MOF-1001**: A solution of $MeNH_2$ (50 μL, 40 wt % in $H_2O$) was mixed with DMF (2 mL) as stock solution A. A solid mixture of BPP34C10DA (3.60 mg, $4.36\times10^{-6}$ mol) and $Zn(NO_3)_2$·4 $H_2O$ (5.25 mg, $2.01\times10^{-5}$ mol) was dissolved in DMF (1.0 mL) in a 4 mL vial. Stock solution A (20 μL) was added to the vial. The vial was capped and placed in an isothermal oven at 65 °C for 24 h. The vial was then removed from the oven and allowed to cool to room temperature naturally. After removal of the mother liquor from the mixture, fresh DMF was added to the vial. Light-yellow, cubic crystals of MOF-1001 were collected and rinsed with DMF (4×1 mL). Yield: 75 %; elemental analysis (evacuated) calcd (%) for $Zn_4O(C_{46}H_{46}O_{14})_3$: C 60.36, H 5.07; found: C 59.49, H 5.07.

**MOF-1002**: A solution of $MeNH_2$ (50 μL, 40 wt % in $H_2O$) was mixed with DMF (2 mL) as stock solution A. A solid mixture of NPP36C10DA (3.82 mg, $4.36\times10^{-6}$ mol) and $Zn(NO_3)_2$·4 $H_2O$ (5.25 mg, $2.01\times10^{-5}$ mol) was dissolved in DMF (1.0 mL) in a 4 mL vial. Stock solution A (20 μL) was added to the vial. The vial was capped and placed in an isothermal oven at 65 °C for 24 h. The vial was then removed from the oven and allowed to cool to room temperature naturally. After removal of the mother liquor from the mixture, fresh DMF was added to the vial. Light-yellow, cubic crystals of MOF-1002 were collected and rinsed with DMF (4×1 mL). Yield: 75 %; elemental analysis (evacuated) calcd (%) for $Zn_4O(C_{50}H_{48}O_{14})_3$: C 62.20, H 5.01; found: C 63.21, H 4.98.

CCDC-738436 (**31**), 742778 (BPP34C10DE), 738435 (NPP36C10DA), 728420 (DMBP·2 $PF_6$⊂BPP34C10DA), 738434 (BPP34C10DE-CAT·4 $PF_6$), 728415 and 728416 (MOF-1001), and 728419 (MOF-1002) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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