Article

Big, Strong, Neutral, Twisted, and Chiral π Acids

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Abstract

General synthetic access to expanded π-acidic surfaces of variable size, topology, chirality, and π acidity is reported. The availability of π surfaces with these characteristics is essential to develop the functional relevance of anion–π interactions with regard to molecular recognition, translocation, and transformation. The problem is that, with expanded π surfaces, the impact of electron-withdrawing substituents decreases and the high π acidity needed for strong anion–π interactions can be more difficult to obtain. To overcome this problem, it is herein proposed to build large surfaces from smaller fragments and connect these fragments with bridges that are composed only of single atoms. Two central surfaces for powerful anion–π interactions, namely, perfluoroarenes and naphthalenediimides (NDIs), were selected as fragments and coupled with through sulfide bridges. Their oxidation to sulfoxides and sulfones, as well as fluorine substitution in the peripheral rings, provides access to the full chemical space of relevant π acidities. According to cyclic voltammetry, LUMO levels range from −3.96 to [...]

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Big, Strong, Neutral, Twisted, Chiral π-Acids

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Abstract: General synthetic access to expanded π-acidic surfaces of variable size, topology, chirality and π-acidity is reported. The availability of π-surfaces with these characteristics will be essential to develop the functional relevance of anion-π interactions with regard to molecular recognition, translocation as well as transformation. The problem is that with expanded π-surfaces, the impact of withdrawing substituents decreases and the high π-acidic needed for strong anion-π interactions can be more difficult to obtain. To overcome this problem, we here propose to build large surfaces from smaller fragments and connect these fragments with bridges that are composed of single atoms only. The two central surfaces for powerful anion-π

interactions were selected as fragments. Namely, perfluoroarenes were coupled with naphthalenediimides via sulfide bridges. Their oxidation to sulfoxides and sulfones, and fluorine substitution in the peripheral rings provides access to the full chemical space of relevant π-acidities. According to cyclic voltammetry, LUMO levels reach from -3.96 to -4.72 eV. With sulfoxide bridges, stereogenic centers are introduced to further enrich the intrinsic planar chirality of the expanded surfaces. The stereoisomers were separated by chiral HPLC and characterized by X-ray crystallography. Their topologies reach from anion-π chairs to anion-π boats, the latter reminiscent of the cation-π boxes in operational neuronal receptors. With pentafluorophenyl acceptors, the π-acidity of NDIs with two sulfoxides in the core reaches -4.45 eV, whereas two sulfones give with -4.72 eV a value that is as low as with four ethylsulfones, a "super-π-acid" near the limit of existence. Beyond anion-π interactions, these conceptually innovative π-acidic surfaces are also of interest as electron transporters in conductive materials.

Introduction

Most π-acids are aromatic rings with electron-deficient surfaces.[1-4] Classical aromatic rings, benzene and beyond, are π-basic because the delocalized π-electrons in the π-cloud assure that aromatic surfaces are intrinsically rich in electrons. To produce π-acidic surfaces, electrons are withdrawn from the central π-cloud into accepting substituents at the periphery of the ring. To quantify π-acidity, the z-component of quadrupole moments has been considered. Π-Acids have $Q_{zz} > 0$, π-bases $Q_{zz} < 0$, the combination of both gives push-pull systems.[5] The use of Q_{zz} to classify π-acids is limited because their calculation is influenced by irrelevant aspects (planar symmetry, substituent topology) and ignores essential ones. Among other parameters such as in-plane dipoles and polarizability, π* orbitals and the energy level of the LUMO are presumably more important than π orbitals and HOMO energies to describe the properties of π-acids. π-Acidic surfaces are interesting because they can attract anions,[1,2] electrons[3] and π-bases.[4] Attractive expressions and applications of these fundamental contacts reach from plant co-

pigmentation, antitumor intercalators, sensing[4] and conductive organic materials[3] to anion binding,[1,2,5] transport[6] and the very recent "anion-π catalysis."[7]

Hexafluorobenzene with a Q_{zz} = +9 B and other perfluoroarenes are among the most popular π-acids.[8] Heterocyclic aromatics have received much attention.[1] Cationic aromatics are arguably more demanding with regard to anion-π interactions because contributions from ion pairing are difficult to subtract.[1] Larger potential π-acids with interesting topologies such as the spherical fullerenes[9] or twisted, chiral perylenediimides[10] receive attention mainly as acceptors and transporters of electrons.[3] Naphthalenediimides (NDIs)[11] are privileged motifs because their intrinsic Q_{zz} = +19 B is very high, their LUMO is very low (-4.00 eV), and both can be easily varied with core substituents. Popular choices to maximize π-acidity are cyano groups[6,7] or sulfones.[7,12] The recently introduced phosphonium substituents appear very promising despite their permanent positive charge.[13] However, NDIs are intrinsically planar. Expansion of their core usually reduces π-acidity because the influence of withdrawing substituents decreases.[11] Moreover, core expanded NDIs usually do not have twisted and

chiral topologies. However, the availability of large, strong, neutral, twisted and chiral π-acids will be the key to further elaborate on the functional relevance of anion-π interactions. In this report, we combine the two central π-acids, NDIs[11] and perfluoroarenes,[8] with sulfur bridges[12,14] to secure facile access to expanded surfaces of precisely variable topology (chair, boat), chirality (central, axial, planar), π-acidity (600 mV), and oriented π-acidity gradients (Figure 1). Sulfur bridges[12,14] were particularly attractive to vary π-acidity with simple and robust redox chemistry, to minimize reductive radical formation at high π-acidity,[1] and, most importantly, to introduce chiral twists on the sulfoxide level.

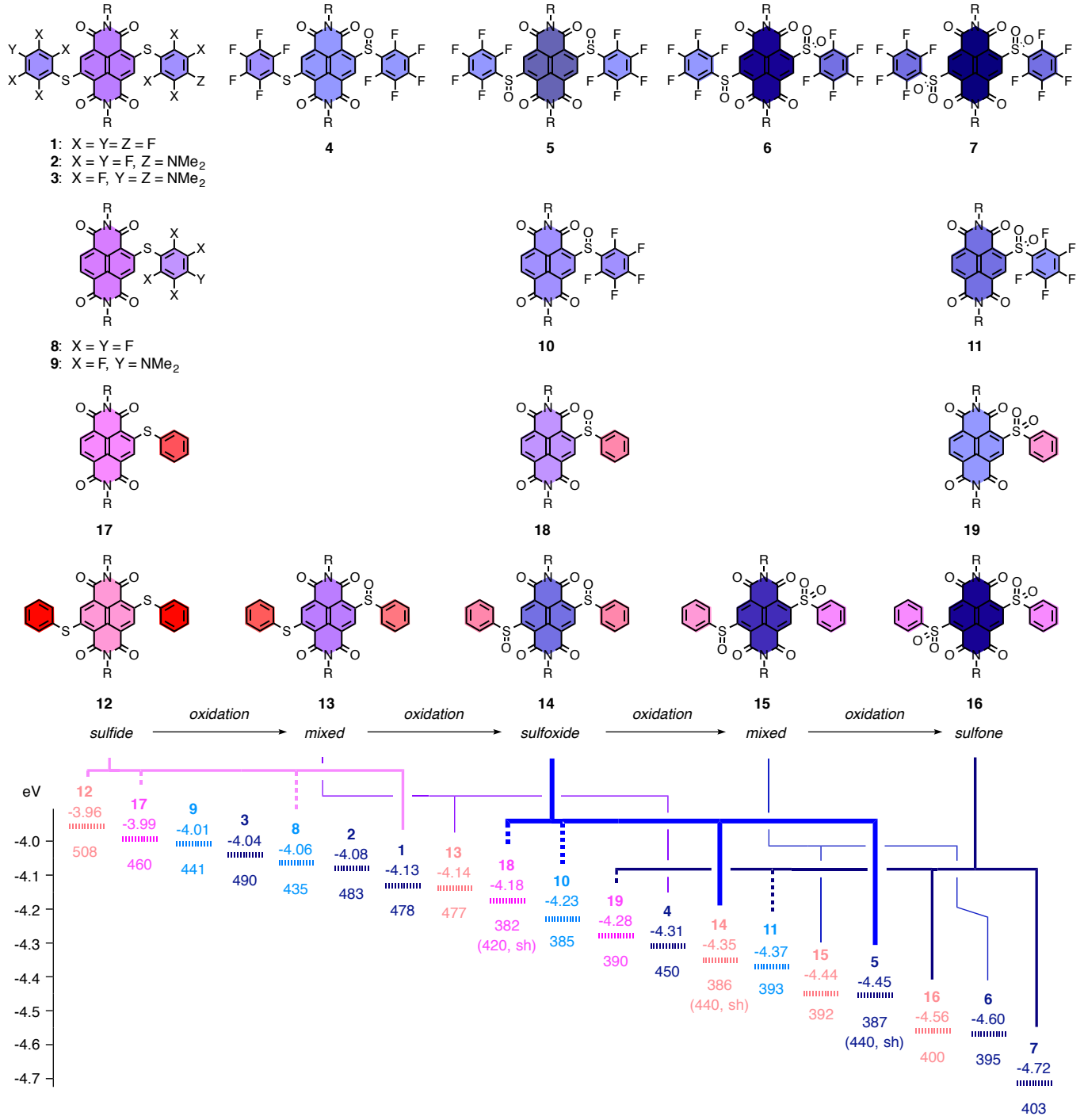
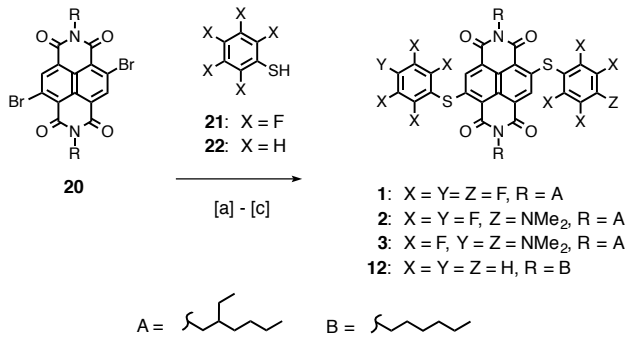


Figure 1. Structure and LUMO energy levels of π-surfaces 1-19 composed of π-acidic NDIs, π-basic phenyls or π-acidic pentafluorophenyls, and sulfur bridges on the oxidation level of sulfide, sulfoxide and sulfone. LUMO energies were obtained by CV and DPV and are reported in eV relative to -5.1 eV for Fc^+/Fc. Values below the dashed line indicating the LUMO levels give the absorption maximum at lowest energy in nanometers, measured in dichloromethane.

Results and Discussion

The collection of π-acids **1**-**19** was prepared from dibromo NDI **20** by nucleophilic substitution with the copper salts of thiophenols **21** and **22** (Figure 1, Scheme 1). The key question of this study was whether or not this reaction would also be possible with the inactivated pentafluorothiophenol **21**. To our delight, this concern turned out to be unjustified. With NMP as a solvent, NDI **1** with two pentafluorophenyl substituents was obtained as the only product. In DMF, NDIs **2** and **3** with one or two dimethylamino donors in para position of the tetrafluorophenyl substituents were isolated as additional products. The same observation was made with monosubstituted NDIs **8** and **9**. The dimethylamino derivatives **2**, **3** and **9** were characterized on the sulfide level but excluded from further oxidation experiments. The other NDIs **1**, **8**, **12** and **17** with one or two phenylsulfides or pentafluorophenylsulfides in the core were gradually oxidized with mCPBA to afford the corresponding sulfoxides and sulfones (Figure 1).



Scheme 1. [a] **21**, DMF, 140 ºC, 12 h, **1**: 27%, **2**: 25%, **3**: 35%, [b] **21**, NMP, 1 h, **1**: 83%, [c] **22**, NMP, 140 ºC, **12**: 82%.

The collection of NDIs was characterized by absorption spectroscopy and cyclic and differential pulse voltammetry. Compared to λ_{abs} = 528 nm for NDIs with two alkylsulfides in the core,[12] the absorption maximum of NDIs with two arylsulfides substituents in the core shifted to the blue

(Figure 1). Strongest blue shifts to λ_{abs} = 475 nm were observed for NDIs **1** with two withdrawing pentafluorophenylsulfides. One or two terminal diamino donors in NDIs **2** and **3** reduced this blue shift to λ_{abs} = 483 nm and λ_{abs} = 495 nm, respectively. NDIs **12** with two phenylsulfides absorbed at λ_{abs} = 510 nm (Figures 1 and 2d). The absorption of NDIs **8** with only one pentafluorophenylsulfide in the core occurred at even shorter λ_{abs} = 435 nm. Terminal dimethylamino donors and phenylsulfides in **9** and **17** caused red shifts up to λ_{abs} = 460 nm.

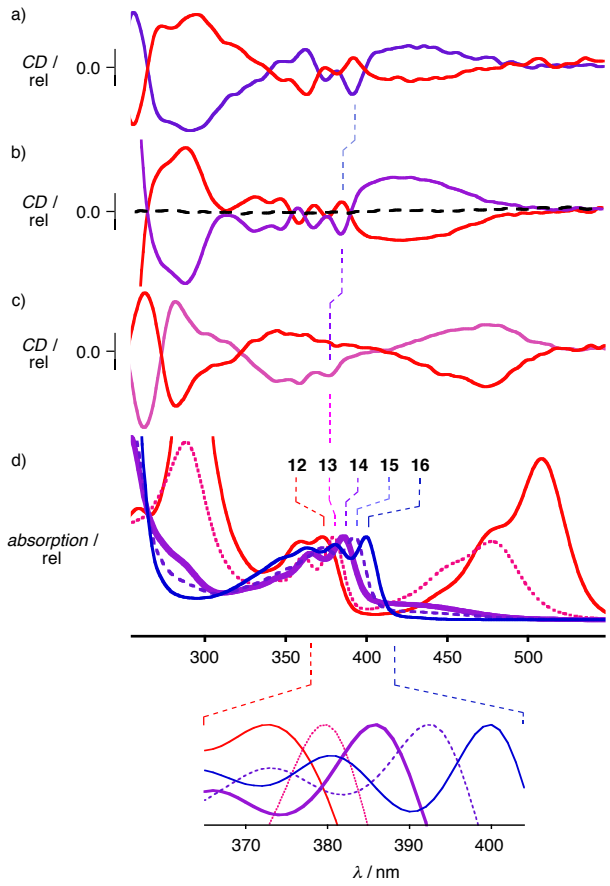


Figure 2. CD spectra of both enantiomers of **15** (a), **14** (b; with the achiral *R,S*-diastereomer, dashed) and **13** (c) in CH_2Cl_2. (d) Absorption spectra of **12**-**16** in CH_2Cl_2, normalized at maxima at 380-410 nm.

NDIs **5** and **14** with two arylsulfoxides in the core showed a shoulder around λ_{abs} = 440 nm (Figures 1 and 2d). This shoulder nearly disappeared for NDIs **10** and **19** with only one arylsulfoxide in the core. The absorption of NDIs with arylsulfones in the core was similar to that of unsubstituted NDIs. Interestingly, the original NDI absorbance below 400 nm showed a nearly linear increase with increasing withdrawing nature of the substituent in the core. For the phenyl series, the absorbance of **12** with two sulfides in the core maximized at λ_{abs} = 373 nm (Figure 2d). Oxidation of only one sulfide into a sulfoxide gave **13** with λ_{abs} = 380 nm. Oxidation of the second sulfide into a sulfoxide gave **14** with λ_{abs} = 386 nm. Oxidation of one sulfoxide into a sulfone gave **15** with λ_{abs} = 392 nm. NDI **16** with two sulfones in the core absorbed exactly at λ_{abs} = 400 nm.

The energy levels of the LUMOs of NDIs **1**-**19** were determined by cyclic (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2 against the Fc^+/Fc couple as internal standard. With two distinct, reversible reduction steps, cyclic voltammograms did not differ in appearance from that of other NDIs.[11,12] The energy of the LUMO against vacuum was calculated assuming -5.1 eV for Fc^+/Fc. The obtained values are summarized in Figure 1. The LUMO level of the NDI **1** with two withdrawing pentafluorophenylsulfides was found at -4.13 eV. Substitution of the two pentafluorophenyl acceptors in **1** by two phenyl donors in **12** increased the LUMO level by +170 meV to -3.96 eV. Removal of one pentafluorophenylsulfide in **1** *increased* the LUMO level by +70 meV to -4.06 eV in monosubstitued **8**. The complementary removal of one phenylsulfide in **12** *decreased* the LUMO level by -30 meV to -3.99 eV in monosubstitued **17**. The resulting increase for substitution from pentafluorophenyl to phenyl with monosubstitued NDIs **8** and **17** was with +70 meV clearly less than half the +170 meV obtained with disubstituted NDIs **1** and **12**.

One or two terminal diamino donors NDI **2** and **3** increased the LUMO level of NDI **1** with two pentafluorophenylsulfides by +50 meV and +90 meV, respectively. The LUMO energy of the intriguing donor-acceptor-donor (DAD) substituted NDI **3** was above that of NDI **8** with only one pentafluorophenylsulfide in the core, near the one of unsubstituted NDI under these conditions (-4.01 eV).

Oxidation of the two sulfides in disubstituted NDIs **12** and **1** to two sulfoxides lowered the LUMO levels by -370 meV and -320 meV to -4.35 eV for **14** and -4.45 eV for **5**, respectively. The resulting decrease in response to the substitution of phenyl donors by pentafluorophenyl acceptors was with -100 meV from **14** to **5** clearly less pronounced on the sulfoxide level than with -170 meV from **12** to **1** on the sulfide level. The with -4.45 eV very strong π-acidity obtained with pentafluorophenyl acceptors in **5** were most important because twist and chirality accessible with sulfoxide bridges are more interesting than the less spectacular topologies obtained with more withdrawing sulfone bridges (see below).

Further oxidation from two sulfoxides to two sulfones lowered the LUMO levels by -210 meV and -220 meV to -4.56 eV for **16** and -4.72 eV for **7**, respectively. This increase in π-acidity was less pronounced than the -320 to -370 meV obtained for the oxidation of sulfides **1** and **12** into sulfoxides **5** and **14**. The -4.72 eV obtained for NDI **7** is remarkable. It is as low as that of tetrasubstituted NDIs with four alkylsulfones in the core. This finding demonstrates that two pentafluorophenylsulfones in the NDI core are sufficient to access "super-π-acids," that is π-acids that are nearly at the limit of π-acidity with still reasonable stability. Disubstituted NDIs with pentafluorosulfones are more attractive super-π-acids than tetrasubstituted NDIs with alkylsulfones, particularly with regard to anion-π catalysis, because they provide access to planar chirality.

The central series of pentafluorophenyl and phenyl NDIs with two sulfide, sulfoxide and sulfone bridges was complemented with the NDIs with mixed bridges (Figure 1). The mixed pentafluorophenyl NDI **4** with one sulfide and one sulfoxide bridge localized with a LUMO at -4.31 eV and a λ_{max} = 450 nm roughly halfway between NDI **1** with two sulfides at -4.15 and 478 nm and NDI **5** with two sulfoxides at -4.45 and 387 nm. The same was true for the mixed pentafluorophenyl NDI **6** with one sulfoxide and one sulfone. The impressive -4.60 eV of NDI **6** was clearly below the -4.45 eV of NDI **5** with two sulfoxides and near the -4.72 eV of NDI **7**, the lowest LUMO of the entire collection. The mixed pentafluorophenyl NDI **6** with one sulfoxide and

one sulfone bridge was even slightly more π-acidic than the phenyl NDI **16** with two sulfones. The mixed phenyl NDIs **13** and **15** followed exactly the same trend, positioned inbetween NDIs **12**, **14** and **16** with two sulfides, sulfoxides and sulfones, respectively.

For completion, the complementary series of pentafluorophenyl and phenyl NDIs with only one sulfide, sulfoxide and sulfone in the core was made and studied as well (Figure 1). The LUMO levels of NDIs **8** and **17** with one sulfide only located between the extreme levels marked by NDIs **1** and **12** with two sulfides in the core. In contrast, NDIs **18**, **10**, **19** and **11** with one sulfoxide and sulfone had clearly higher LUMO levels than their disubstituted counterparts **14**, **5**, **16** and **7**, independent of the nature of the phenyl group.

Taken together, the coupling of phenyl and NDI planes by sulfur bridges on the sulfide, sulfoxide and sulfone level provided access to gradually decreasing LUMO levels from -3.96 eV to -4.72 eV, covering a range of 760 meV in a redox cascade of 19 discrete steps. The diversity of realized combinations is best illustrated in the four corners of Figure 1. Highest π-acidity in core and periphery is realized in **7** in the top right corner, highest π-basicity in **12** in the bottom left corner. NDI **16** in the bottom right corner has a π-acidic core and a π-basic periphery, NDI **1**, top left, shows the complementary outward gradient with a π-acidic periphery.

However, the intermediate NDIs **4**-**6**, **10**, **13**-**15** and **18** with one or two sulfoxides in the core are arguably most attractive members of the collection because of their interesting topology (Figures 1 and 3). For the phenyl series, all sulfoxide stereoisomers of **13**-**15** and **18** were separated by chiral column chromatography. The circular dichroism (CD) spectra of NDIs **13**-**15** with chiral sulfoxides gave very weak CD Cotton effect with interesting pattern, including well resolved vibronic finestructures for the absorption below 400 nm (Figure 2, a-c). All pairs of enantiomers gave the expected mirror-imaged CD spectra. The *R*,*S* enantiomer of NDI **14** with two sulfoxides in the core was CD inactive as expected for an achiral *meso* compound (Figure 2b, dashed).

Absolute configurations were assigned by X-ray crystallography. The crystal structure of *SS*-**14** confirmed[12] that the S=O bonds are oriented more or less in plane of the naphthalene to assure full conjugation and turned away from the repulsive imide carbonyls. This conformation positions the π-basic phenyl planes almost perpendicular to the π-acidic NDI plane. Plane-to-plane angles in this "boat" or "*cis*" structure of 98.2º and 101.6º were measured, possibly influenced by intermolecular face-to-face stacking of another phenyl π-base on the NDI π-acid. Similar plane-to-plane angles were found in energy-minimized molecular models of *SS*-**14** (Figure 3e). The ground state geometries were optimized with the Gaussin09 program[15] using M06-2X functional[16,17] and 6-311G** basis set. All minima were characterized by the vibrational analysis with all frequencies being positive. In *SS*-**5**, the pentafluorophenyl planes were slightly twisted because of F-O repulsions from the imide carbonyls (Figure 3c). These boat topologies provide an attractive starting point for architectures reminiscent of the cation-π box in neural receptors[18] with alternating strong and weak π-acidity in *SS*-**14** (Figure 3e, blue and green) and homogenously strong π-acidity in *SS*-**5** (Figure 3c, blue).[19]

The crystal structure of *meso*-**14** revealed the complementary "chair" or "*trans*" arrangement (Figure 3b). As with the boat structure of *SS*-**14**, the chair structure of *meso*-**14** originates from the conjugation of the S=O bonds with the naphthalene core. The π-basic phenyl planes remain quasi perpendicular to the naphthalene plane, but is turned upward and the other downward. The resulting topology is reminiscent of the chair conformer of cyclohexanes, although the "chair design" has more a touch of modern art. Electron potential surfaces of *meso*-**5** revealed a twisted π-surface of homogenously strong π-acidity (Figure 3d). The complementary EPS surface of *meso*-**14** illustrated the inward π-acidity gradient present on the same twisted surface (Figure 3f). These chair isomers will be most interesting to create chiral space once that symmetry is broken with different imide substituents ($R^1 \neq R^2$). Synthetic access toward this chiral space offered by

chair or "*trans*" isomers of **5** and **14** will be attractive to realize the so far elusive asymmetric anion-π catalysis.[7]

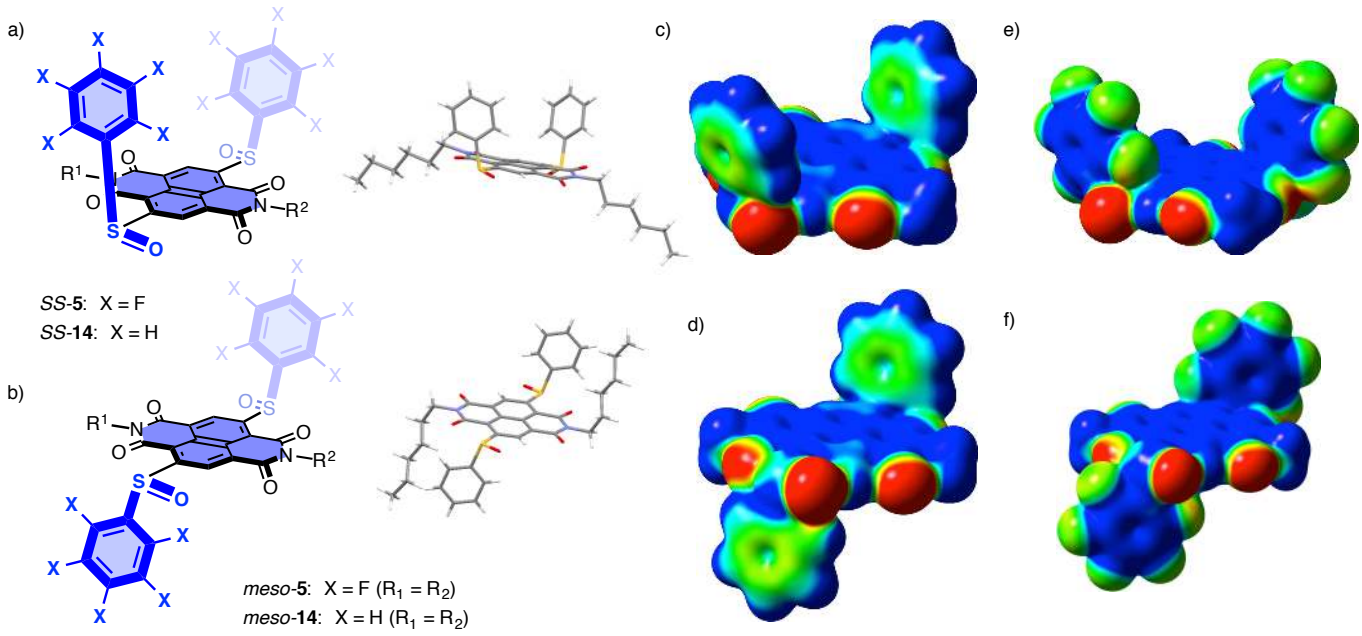


Figure 3. Crystal structures (a, b) and electron surface potentials (c-f) of sulfoxide bridged stereoisomers *SS*-14 (a, e), *meso*-14 (b, f), *SS*-5 (c) and *meso*-5. The computed MP2/6-311G**//M062X/6-311G** electrostatic potential (±19 kcal mol^{-1}) was defined by the 0.005 au electronic density contour,[19] blue = π-acidic, red = π-basic.

Conclusions

The objective of this study was to explore the coupling of pentafluorophenyl and naphthalenediimide planes with sulfur bridges as general approach to expand π-acidic surfaces toward chiral 3D topologies. This fragment approach is proposed to secure access to expanded and twisted π-surfaces without losses in π-acidity. The resulting series covers LUMO levels within 760 meV, from -3.96 eV to -4.72 eV, with a redox cascade of 19 discrete levels. Homogenously π-acidic and π-basic surfaces are as accessible as surfaces with inward or outward π-acidity gradients. The most complex DADADAD pattern with amino donors at the end of tetrafluorophenyl acceptors bridged with sulfide donors to central NDI acceptors as in **3** is

promising with regard to conductive materials.[3] "Super-π-acids" such as **7** with -4.72 eV are attractive for applications because of their expanded surface as well as the planar chirality that is accessible with disubstituted but not with tetrasubstituted NDIs. Most intriguing are the folded, chair and boat shaped topologies obtained with chiral sulfoxide bridges. These important topologies are available as continuously strong π-acids as in **5** or with inward directed π-acidity gradients as in **14**. With withdrawing perfluoroarene substituents, strong π-acidity, -445 meV below the native NDI, sufficient for significant anion-π interactions, can be obtained also with chiral disulfide bridges. These twisted and chiral architectures will be very interesting for use in ionpair-π[5] and anion-π catalysis.[7] Intense studies in this direction are ongoing and will be reported in due course.

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