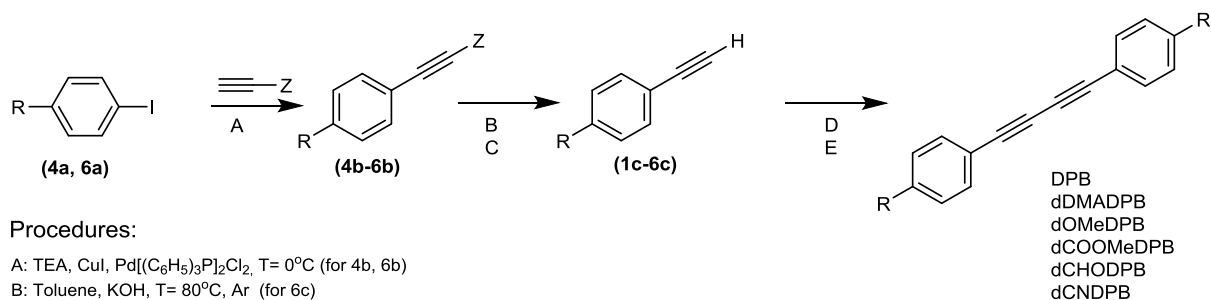


Experimental and theoretical studies of spectroscopic properties of
simple symmetrically substituted diphenylbuta-1,3-diyne derivatives

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Procedures:

A: TEA, CuI, Pd[(C₆H₅)₃P]₂Cl₂, T= 0°C (for 4b, 6b)

B: Toluene, KOH, T= 80°C, Ar (for 6c)

C: DMF, KF, T=20°C (for 4c, 5c)

D: DMF, CuI, T= 55°C, Ar (DPB, dOMeDPB, dCOOMeDPB, dCHODPB, dCNDPB)

E: Piridine/methanol, Cu(OAc)₂, T=20°C dDMADPB

-R	-Z
-H (1)	-
-N(CH ₃) ₂ (2)	-
-OCH ₃ (3)	-
-COOCH ₃ (4)	-TMS
-CHO (5)	
-CN (6)	-C(CH ₃) ₂ (OH)

Scheme 1. Synthesis of diphenylbuta-1,3-diyne derivatives.

General procedure

Protected acetylene derivatives were synthesized according to Sonogashira-Hagihara procedure¹⁻⁴.

Synthesis of symmetrically of diphenylbuta-1,3-diyne derivatives were based on Glaser⁵⁻⁶ (DPB, (CH₃OPh)₂DA, (CH₃O₂CPh)₂DA, (OHCHPh)₂DA, (NCPH)₂DA)) (procedure D) or Eglinton⁷⁻⁸ (DMAPh)₂DA (procedure E) methods.

Methyl-4-iodobenzoate, 4-iodobenzonitrile, 4-((trimethylsilyl)ethynyl)benzaldehyde, phenylacetylene, 4-ethynylanisole, 4-ethynyl-N,N-dimethylaniline, ethynyltrimethylsilane, bis(triphenylphosphine)palladium(II) dichloride (Sigma Aldrich), 2-methyl-3-butyn-2-ol (Fluka) were commercially available and used without further purification.

Synthesis of protected acetylene derivatives

Procedure A

Methyl 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate (4b) and 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzotrile (6b) were prepared according to Sonogashira-Hagihara coupling reaction¹⁻⁴ of appropriate acetylene derivatives with the respective halogenoarenes.

Appropriate halogenoarene (1 eq) was dissolved in triethylamine (TEA) and the solution was cooled to 0°C. Then trace amount of copper iodide and bis(triphenylphosphine)palladium(II) dichloride, (Pd[(C₆H₅)₃P]₂Cl₂) as catalysts were added. After a few minutes acetylene derivatives: ethynyltrimethylsilane (for 4b) and 2-methyl-3-butyn-2-ol (1 eq) (for 6b) was added. Progress of reaction was monitored by TLC. The reaction mixture was stirred for 8-12 h and if it was need for 24 h in temperature room. Then reaction mixture was filtered and extracted into ethyl acetate and washed with water. Combined organic layers were dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated. The pure products were isolated by column chromatography on silica gel (petroleum ether/ethyl acetate; 7:1 (4b), 10:1 (6b)).

Removing the protective groups (procedure B and C)

Procedure B

A mixture of 6b (1eq) and potassium hydroxide (1eq) in toluene was refluxed for 2 h under argon. Progress of reaction was monitored by TLC. The reaction mixture was cooled, filtered, extracted with ethyl acetate and washed with KHSO₄ and water. Combined organic layers were dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated⁹⁻¹⁰. The pure product 4-ethynylbenzotrile (6c) was isolated by multiple crystallization with mixture petroleum ether and ethyl acetate.

Procedure C

Compound 4b or 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzaldehyde (5b) (1eq) was dissolved in dimethylformamid (DMF) and potassium fluoride (3eq) was added¹¹. The reaction was stirred under argon atmosphere at room temperature for 1,5 h. Progress of reaction was monitored by TLC. The reaction mixture was extracted with ethyl acetate and washed with water. Combined organic layers were dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated. The pure products methyl 4-ethynylbenzoate (4c) and 4-ethynylbenzaldehyde (5c) were isolated by multiple crystallization with mixture petroleum ether and ethyl acetate.

Synthesis of symmetrically bisacetylene (procedure D and E)

Procedure D

Appropriate compound (ethynylbenzene (1c), 1-ethynyl-4-methoxybenzene (3c), 4c, 5c, 6c) was dissolved in DMF and stirred under argon atmosphere at about 55°C. After few minutes trace amount of copper iodide as the catalyst was added³. The reaction mixture was stirred for couple of days. Progress of reaction was monitored by TLC. After the reaction was completed crude product was filtered, extracted into toluene and washed with water. Combined organic layers were dried over anhydrous magnesium sulfate and filtered. The pure products were isolated: by crystallization with hot petroleum ether (DPB) or mixture ethyl acetate and petroleum ether ((CH₃OPh)₂DA, (CH₃O₂CPh)₂DA, (NCPh)₂DA)), by column chromatography on silica gel (petroleum ether/ethyl acetate; 10:1) ((OHCPH)₂DA).

Procedure E

4-ethynyl-N,N-dimethylaniline (2c) (1eq) was added to a solution of Cu(OAc)₂·H₂O (2eq) in pyridine and methanol (v/v 1/1) at room temperature under nitrogen⁴. Progress of reaction was monitored by TLC. After couple of days crude product was

filtered, extracted into toluene and washed with water. Combined organic layers were dried over anhydrous magnesium sulfate and filtered. The pure product (DMAPh)₂DA was isolated by means RP-HPLC.

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- [3] S. Thorand, N. Krause, J. Org. Chem., 63, 1998, 8551
- [4] G. Menchi, A. Scrivanti, U. Matteoli, J. Mol. Catal. A:Chem., 152, 1999, 77
- [5] Glaser, C. Ber. Dtsch. Chem. Ges., 2, 1869, 422
- [6] Y. Nishihara, K. Ikegashira, K. Hirabayashi, J. Ando, A. Mori, T. Hiyama, J. Org. Chem., 65, 2000, 1780
- [7] G. Eglinton, A.R. Galbraith, Chem. Ind. (London), 1956, 737;
- [8] G. Eglinton, A.R. Galbraith, J. Chem. Soc., 1959, 889
- [9] G. Rodriguez, J.L. Tejedor, T. La Parra, C. Díaz, Tetrahedron, 62, 2006, 3355
- [10] Q. Xiao, R.T. Ranasinghe, A.M.P. Tang, T. Brown, Tetrahedron, 63, 2007, 3483
- [11] Meijere, S. Kozhuskov, T. Haumann, R. Boese, C. Puls, M. J. Cooney, L. T. Scott, Chem. Eur. J., 1, 1995, 124

Identification data for all compounds studied.

1,4-diphenylbuta-1,3-diyne (DPB) (yield 94%)

¹H-NMR (500 MHz, CDCl₃):

δ_H (ppm): 7.34-7.42 (m, 6H, C⁵H, C⁶H, C⁷H, C^{5'}H, C^{6'}H, C^{7'}H); 7.56 (d, 4H, C⁴H, C⁸H, C^{4'}H, C^{8'}H, J=8 Hz);

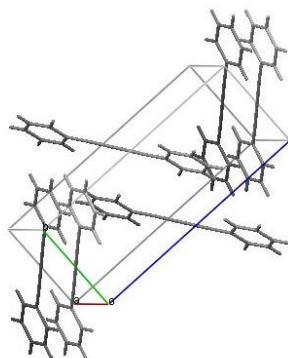
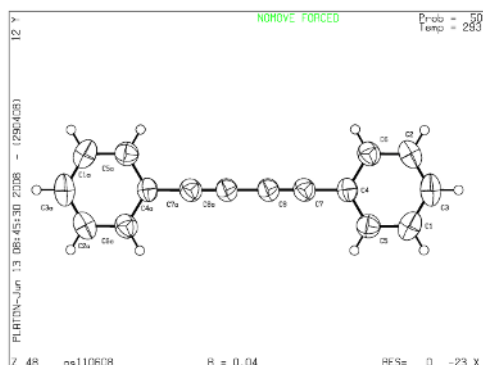
¹³C-NMR (100 MHz, CDCl₃)

δC (ppm): 74.15 $\text{C}^1, \text{C}^{1'}$; 81.8 $\text{C}^2, \text{C}^{2'}$; 122.05 $\text{C}^3, \text{C}^{3'}$; 128.70 $\text{C}^5, \text{C}^7, \text{C}^{5'}, \text{C}^{7'}$; 132.76 $\text{C}^4, \text{C}^8, \text{C}^{4'}, \text{C}^{8'}$;

MS (m/z): 202 (M), 203 (M+H)⁺

Ramman ν_{max} (cm^{-1}): 2215.6 $\text{C}\equiv\text{C}$

crystal structure in accordance with literature data¹²⁻¹⁵:



[12] J.K.D.Surette, M.-A.MacDonald, M.J.Zaworotko, R.D.Singer, J.Chem.Cryst., 24, 1994, 715

[13] R.Thomas, S.S.Mallajyosula, S.Lakshmi, S.K.Pati, G.U.Kulkarni, J.Mol.Struct., 922, 2009, 46

[14] Min Shi, Hen-Xin Qian, Appl.Organomet.Chem, 20, 2006, 771

[15] F.R.Fronczek, M.S.Erickson, J.Chem.Cryst., 25, 1995, 737

4,4'-(buta-1,3-diyne-1,4-diyl)bis(N,N-dimethylaniline) ((DMAPh)₂DA) (yield 36%)

¹H-NMR (500 MHz, CDCl₃):

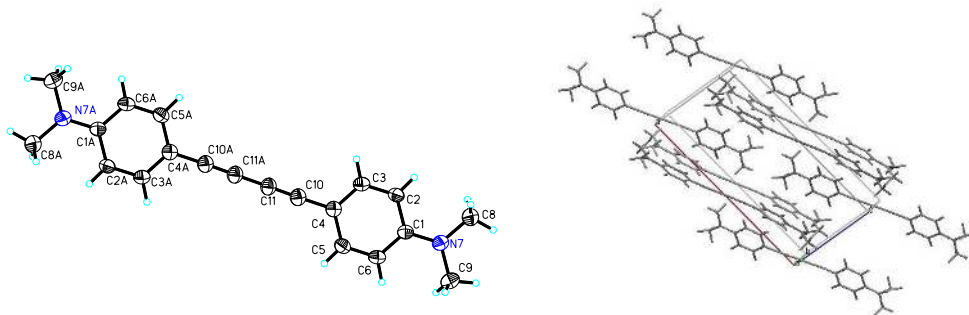
δH (ppm): 2.99 (s, 12H, (CH₃)₄); 6.62 (d, 4H, $\text{C}^4\text{H}, \text{C}^8\text{H}, \text{C}^{4'}\text{H}, \text{C}^{8'}\text{H}$, J=8,8 Hz); 7.39 (d, 4H, $\text{C}^5\text{H}, \text{C}^7\text{H}, \text{C}^{5'}\text{H}, \text{C}^{7'}\text{H}$, J=8.8 Hz);

¹³C-NMR (100 MHz, CDCl₃): 40.15 (CH₃)₄, 72.67 $\text{C}^1, \text{C}^{1'}$; 82.42 $\text{C}^2, \text{C}^{2'}$; 108.76 $\text{C}^3, \text{C}^{3'}$, 111.77 $\text{C}^5, \text{C}^7, \text{C}^{5'}, \text{C}^{7'}$; 133.70 $\text{C}^4, \text{C}^8, \text{C}^{4'}, \text{C}^{8'}$, 150.36 $\text{C}^6, \text{C}^{6'}$

MS (m/z): 289 (M+H)⁺

Ramman $\nu_{\max}(\text{cm}^{-1})$: 2305 $\text{C}\equiv\text{C}$

crystal structure in accordance with literature data¹⁶:



[16] J.G.Rodríguez, S.Ramos, R.Martin-Villamil, I.Fonseca, A.Albert, J.Chem.Soc.,
Perkin Trans.1 ,1996, 541

1,4-bis(4-methoxyphenyl)buta-1,3-diyne ((CH₃OPh)₂DA) (yield 72%)

¹H-NMR (500 MHz, CDCl₃):

δ_{H} (ppm): 3.80 (s, 6H, (OCH₃)₂), 6.82 (d, 4H, C⁵H, C⁷H, C^{5'}H, C^{7'}H, J=8.79 Hz);

J=8.79 Hz); 7.45 (d, 4H, C⁴H, C⁸H, C^{4'}H, C^{8'}H, J=8.30 Hz);

¹³C-NMR (100 MHz, CDCl₃): 55.35 (OCH₃)₂, 72.96 C¹,C^{1'}; 81.18 C²,C^{2'}; 113.92

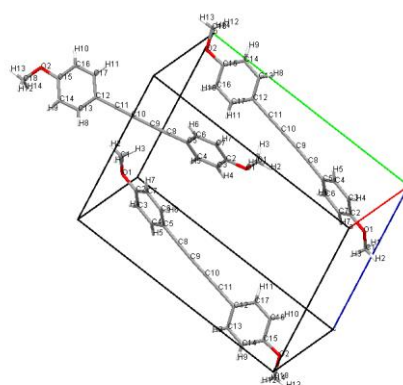
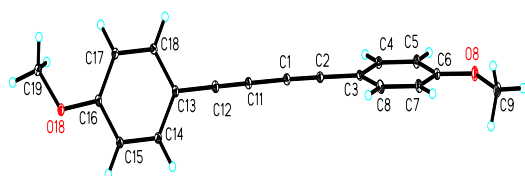
C⁵,C⁷,C^{5'}, C^{7'}; 114.15 C³,C^{3'}; 134.05 C⁴, C⁸, C^{4'},C^{8'}, 160.20 C⁶, C^{6'}

MS (m/z): 262 (M), 263 (M+H)⁺

Ramman $\nu_{\max}(\text{cm}^{-1})$: 2136.8 $\text{C}\equiv\text{C}$

anal. calc. for C₁₈H₁₄O₂ (%): C, 82.45; H, 5.38; found: C, 82.92; H, 5.51

crystal structure in accordance with literature data¹⁷:



[17] Neng-Fang She, Hui-Zhen Guo, Li-Ping Cao, Meng Gao, Acta Crystallogr. Sect. E: Struct. Rep. Online , 62, 2006, 4958

dimethyl 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoate ((CH₂O₂CPh)₂DA) (yield 42%)

¹H-NMR (500 MHz, CDCl₃):

δ_H (ppm): 3.93 (s, 6H, (OCH₃)₂); 7.59 (d, 4H, C³H, C⁷H, C^{3'}H, C^{7'}H, J= 10 Hz); 8.11 (d, 4H, 4H, C⁴H, C⁶H, C^{4'}H, C^{6'}H, J= 10 Hz)

¹³C-NMR (100 MHz, CDCl₃)

δ_C (ppm): 52.5 (OCH₃)₂; 77.01 C¹, C^{1'}, 82.00 C², C^{2'}; 126.74 C³, C^{3'}; 130.0 C⁴, C⁸, C^{4'}, C^{8'}, 131.71 C⁵, C⁷, C^{5'}, C^{7'}; 133.9 C⁶, C^{6'}; 167.0 C⁹, C^{9'};

MS (m/z): 319 (M+H)⁺

Ramman ν_{max}(cm⁻¹): 2219 C≡C

4,4'-(buta-1,3-diyne-1,4-diyl)dibenzaldehyde ((OHCPH)₂DA) (yield 29 %)

¹H-NMR (500 MHz, CDCl₃):

δ_H (ppm): 7.72 (d, 4H, C⁴H, C⁸H, C^{4'}H, C^{8'}H, J= 10 Hz); 7.90 (d, 4 H, C⁵H, C⁷H, C^{5'}H, C^{7'}H, J= 10 Hz); 10.05 (s, 2H, (C⁹H, C^{9'}H))

¹³C-NMR (100 MHz, CDCl₃)

δ_C (ppm): 75.40 C¹, C^{1'}; 83.01 C², C^{2'}; 128.12 C³, C^{3'}; 130.00 C⁴, C⁸, C^{4'}, C^{8'}; 133.28 C⁵, C⁷, C^{5'}, C^{7'}; 136.07 C⁶, C^{6'}; 191.98 C⁹, C^{9'}

MS (m/z) : 259 (M+H)⁺

Ramman ν_{\max} (cm⁻¹): 2214 C≡C

4,4'-(buta-1,3-diyne-1,4-diyl)dibenzonitrile ((NCPH)₂DA) (yield 36 %)

¹H-NMR (500 MHz, CDCl₃):

δ_H (ppm): 7.59-7.67 (q, 8 H, C⁴H, C⁸H, C^{4'}H, C^{8'}H, C⁵H, C⁷H, C^{5'}H, C^{7'}H, J= 10 Hz, J= 10 Hz);

¹³C-NMR (100 MHz, CDCl₃):

δ_C (ppm): 78.02 C¹, C^{1'}; 81.63 C², C^{2'}; 113.20 C⁶, C^{6'}; 118.24 C⁹, C^{9'}; 126.35 C³, C^{3'}; 132.28 C⁵, C⁷, C^{5'}, C^{7'}; 133.24 C⁴, C⁸, C^{4'}, C^{8'};

MS (m/z) : 252 (M)

Ramman ν_{\max} (cm⁻¹): 2233 C≡C

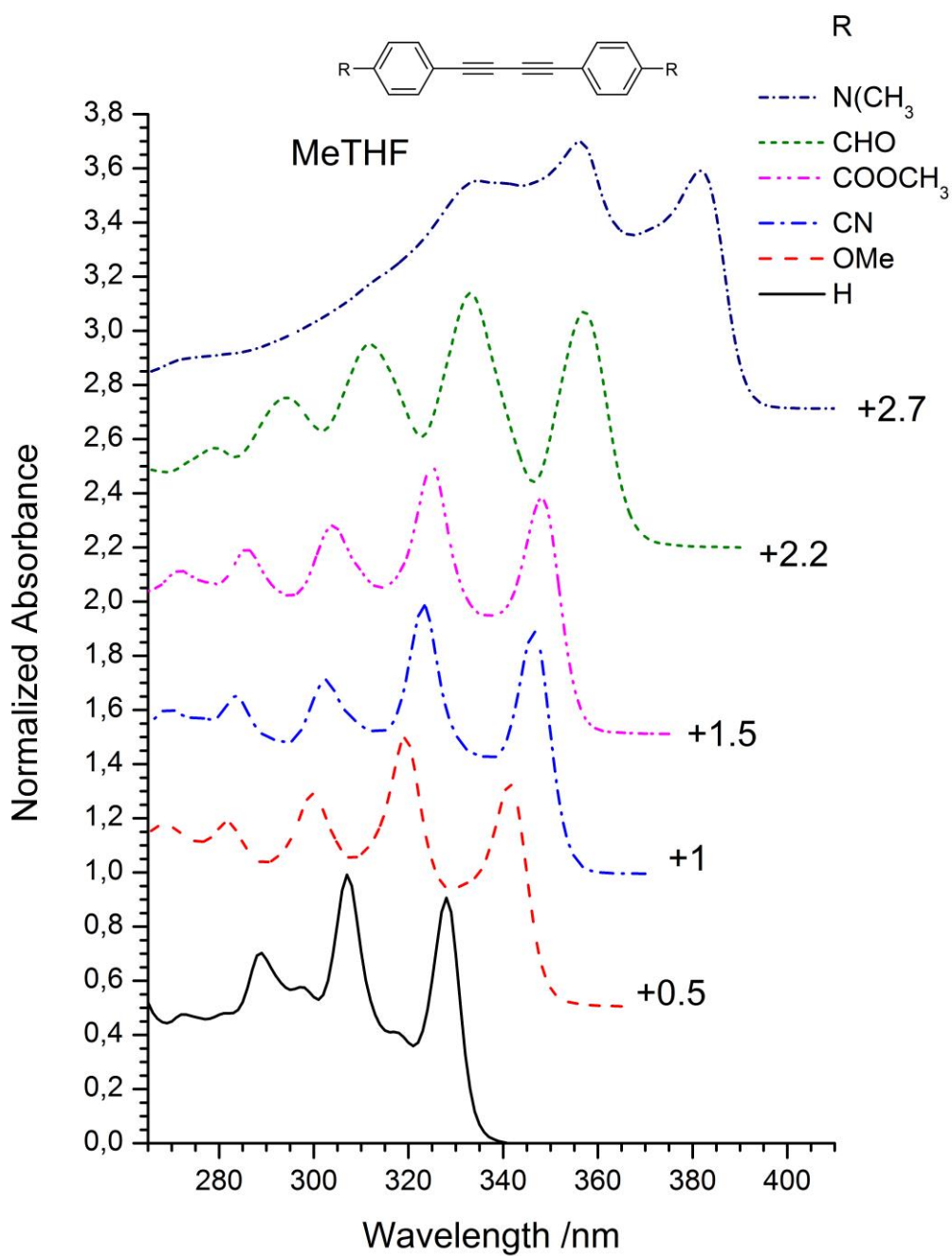


Fig. 1 ESI Absorption spectra of DPB derivatives measured in 2-methyltetrahydrofuran.

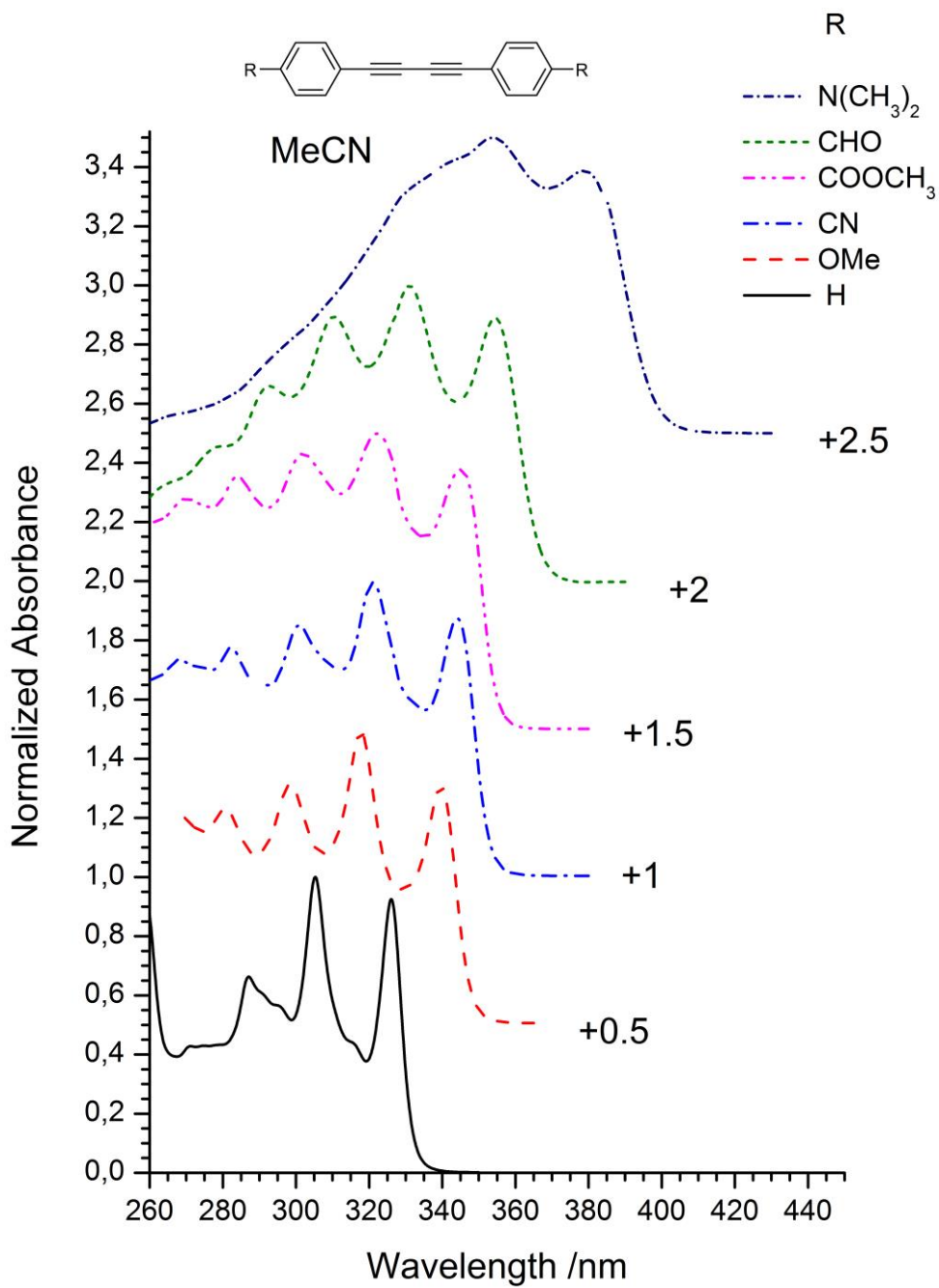


Fig. 2 ESI Absorption spectra of DPB derivatives measured in acetonitrile.

Table 1 ESI Absorption wavelength (λ_{abs}) and molar absorption coefficient (ϵ) of diphenylbuta-1,3-diyne derivatives in selected solvents.

Compound	Solvent	λ_{abs} (nm)	ϵ (dm ³ mol ⁻¹ cm ⁻¹)
DPB	MeCN	287	16695
		305	25147
		326	23184
	cyclohexane	288	17636
		307	27794
		328	25491
	C ₆ H ₁₄	290	19939
		308	28307
		329	25919
	C ₁₆ H ₃₄	289	14307
		307	20024
		328	18408
	MeTHF	289	10376
		307	14473
		328	13370
	MCH	288	12004
		307	17802
		328	16267
(DMAPh) ₂ DA	MeCN	329	16497
		354	20029
		379	17804
	cyclohexane	327	19759
		347	21340
		373	19649
	C ₆ H ₁₄	323	19649
		345	21173
		370	19874
	C ₁₆ H ₃₄	326	20196
		348	21340
		374	19759
	MTHF	341	22208
		354	25089
		377	24819
	MCH	324	19810
		346	23186
		372	20794
(CH ₃ OPh) ₂ DA	MeCN	298	15327
		318	18864
		340	15425
	cyclohexane	300	16074
		318	21305
		340	18220
	C ₆ H ₁₄	296	10493
		316	13629
		338	11185
	C ₁₆ H ₃₄	298	10540
		318	13185
		340	10745
	MeTHF	300	17669
		318	15673
		340	12183
	MCH	297	13983
		317	17170
		339	13779

(CH ₃ O ₂ CPh) ₂ DA	MeCN	284	26175
		302	28716
		322	30753
		345	27024
	cyclohexane	286	29560
		303	30753
		325	32794
348		29206	
C ₆ H ₁₄	284	29422	
	302	30399	
	322	31808	
	346	28500	
C ₁₆ H ₃₄	286	25548	
	304	27731	
	325	30753	
	348	27307	
Me-THF	294	21753	
	312	28786	
	333	31946	
MCH	357	19367	
	285	19221	
	303	21125	
	325	27660	
(OHCPH) ₂ DA	MeCN	348	24638
		292	10987
		310	14671
		331	15588
	cyclohexane	355	13932
		294	5430
		312	7488
333		8630	
C ₆ H ₁₄	358	8077	
	292	1741	
	310	2825	
	331	3406	
C ₁₆ H ₃₄	356	3185	
	295	2190	
	312	3479	
	334	4253	
MeTHF	358	4033	
	294	9772	
	312	13235	
	333	16691	
MCH	357	15519	
	293	3003	
	311	3812	
	332	4470	
(NCPH) ₂ DA	MeCN	356	3959
		300	14426
		321	16833
		344	14868
	cyclohexane	302	5597
		323	9364
		346	8578
C ₆ H ₁₄	302	4105	
	323	5581	
	347	4151	
C ₁₆ H ₃₄	302	3527	
	323	4643	
	347	3566	

	MeTHF	302	16539
		323	23031
		346	20624
	MCH	302	4151
		322	5380
		346	4597

Table 2 ESI The solvatochromic shift of absorption spectra of 4,4` substituted diphenylbuta-1,3-diyne derivatives.

	MCH λ /nm	MeTHF λ /nm	MeCN λ /nm
-H	328	328	326
-OMe	339.5	341	339.5
-CN	346.5	346.5	344
-COOMe	348	348	345
-CHO	357	357	354.5
-DMA	372	382	379

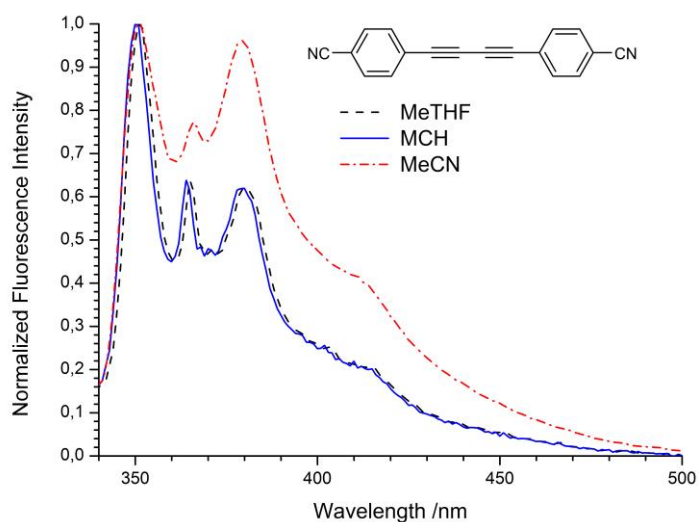


Fig. 3 ESI Fluorescence spectra of (NCPH)₂DA in 2-methyltetrahydrofuran (black dashed line), methylcyclohexane (blue solid line) and acetonitrile (red dash-dot line).

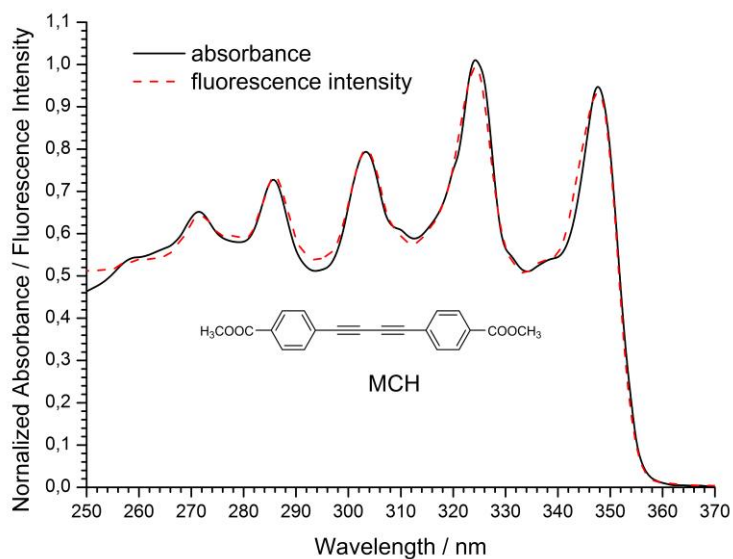


Fig. 4 ESI Absorption (black solid line) and fluorescence excitation spectrum (red dashed line) of $(\text{CH}_3\text{O}_2\text{CPh})_2\text{DA}$ in methylcyclohexane.

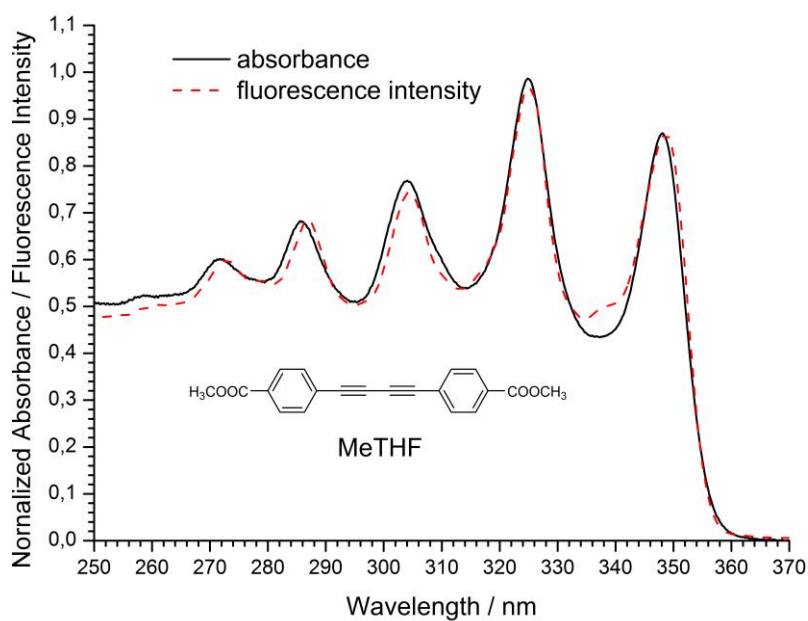


Fig. 5 ESI Absorption (black solid line) and fluorescence excitation spectrum (red dashed line) of $(\text{CH}_3\text{O}_2\text{CPh})_2\text{DA}$ in 2-methyltetrahydrofuran.

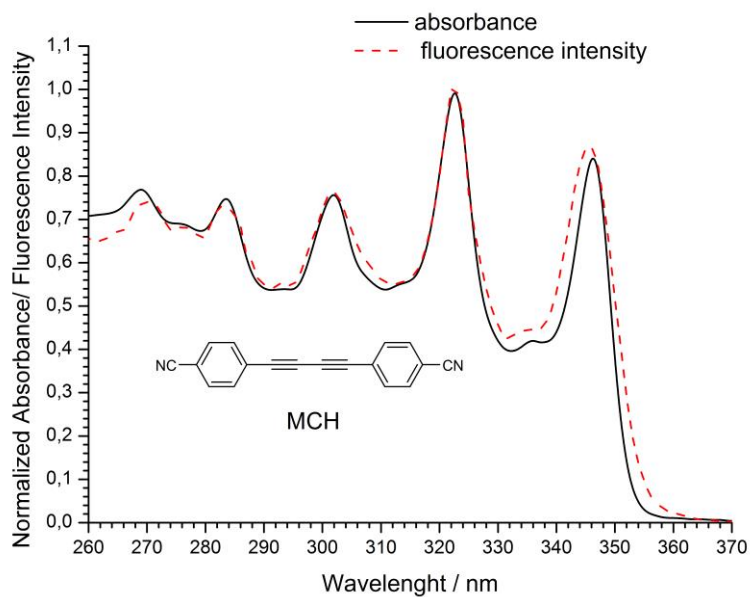


Fig. 6 ESI Absorption (black solid line) and fluorescence excitation spectrum (red dashed line) of (NCPH)₂DA in methylcyclohexane.

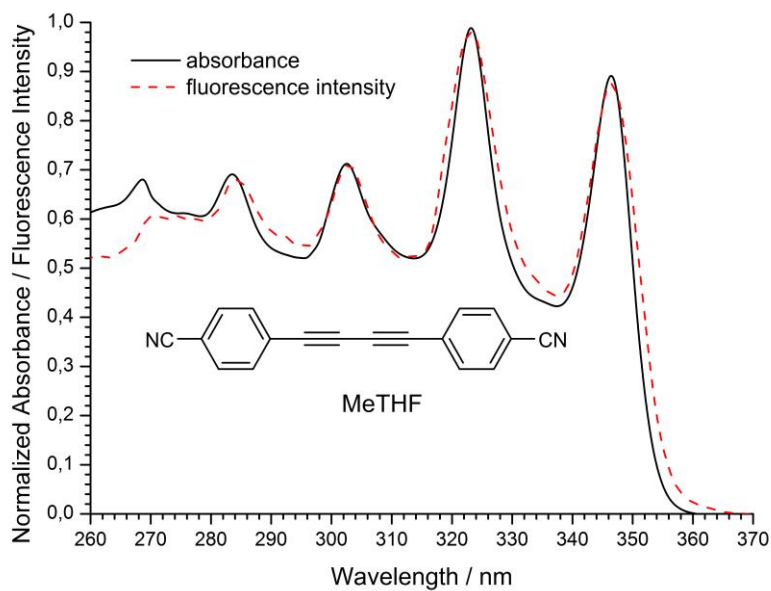


Fig. 7 ESI Absorption (black solid line) and fluorescence excitation spectrum (red dashed line) of (NCPH)₂DA in 2-methyltetrahydrofuran.

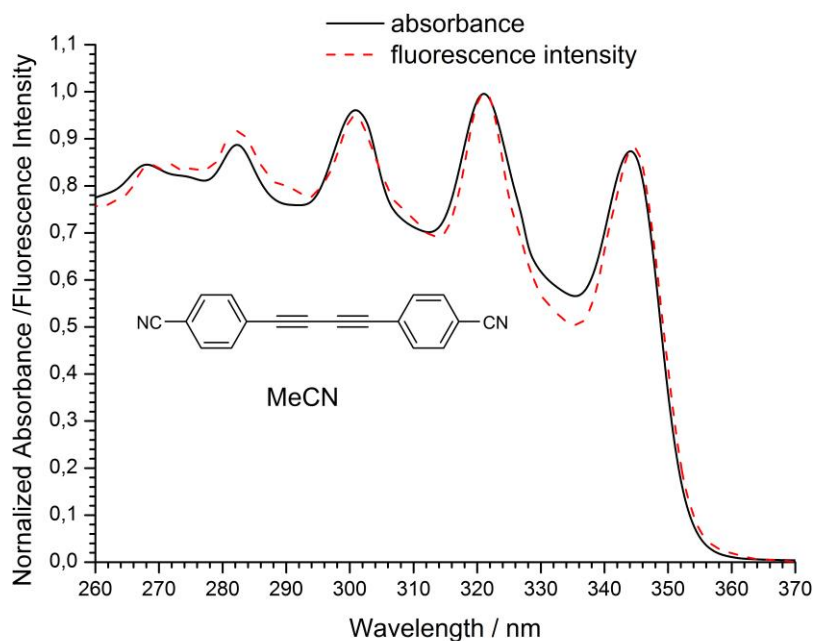


Fig. 8 ESI Absorption (black solid line) and fluorescence excitation spectrum (red dashed line) of (NCPH)₂DA in acetonitrile.

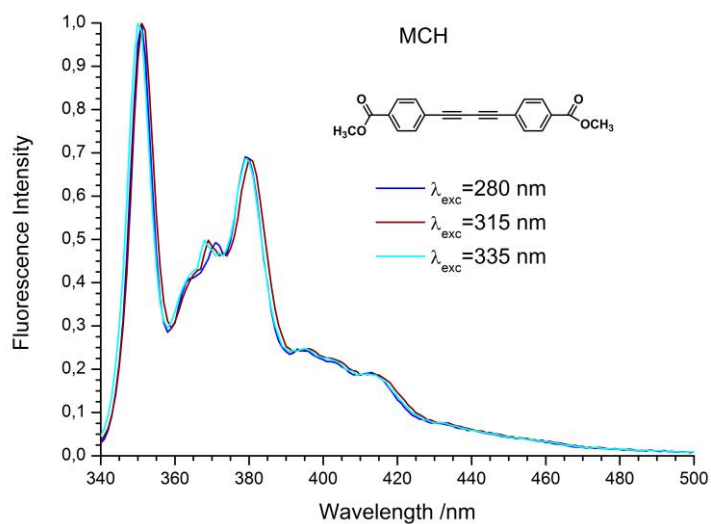


Fig. 9 ESI Fluorescence spectra of (CH₃O₂CPh)₂DA in methylcyclohexane recorded at different excitation wavelength. Fluorescence quantum yield for excitation wavelength $\lambda_{\text{exc}}=280$ nm is equal to 0.0142, for $\lambda_{\text{exc}}=315$ 0.0137 and for $\lambda_{\text{exc}}=335$ 0.0140.

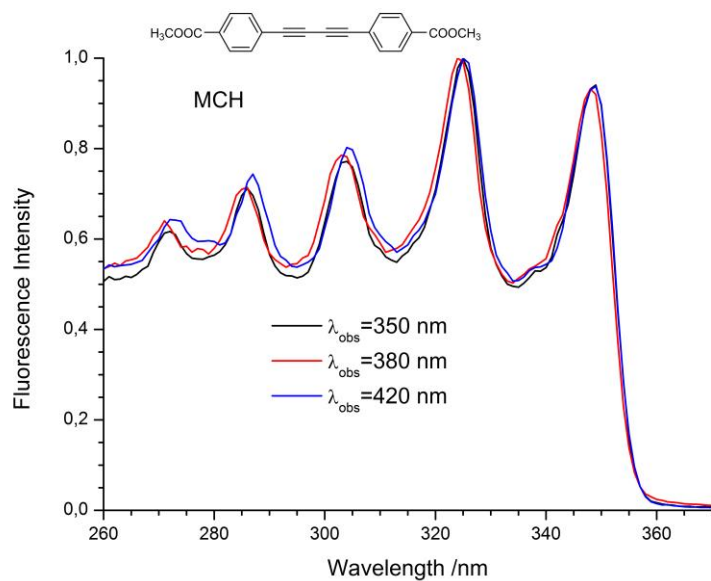


Fig. 10 ESI Fluorescence excitation spectra of (CH₃O₂CPh)₂DA in ethylcyclohexane at different observation wavelength.

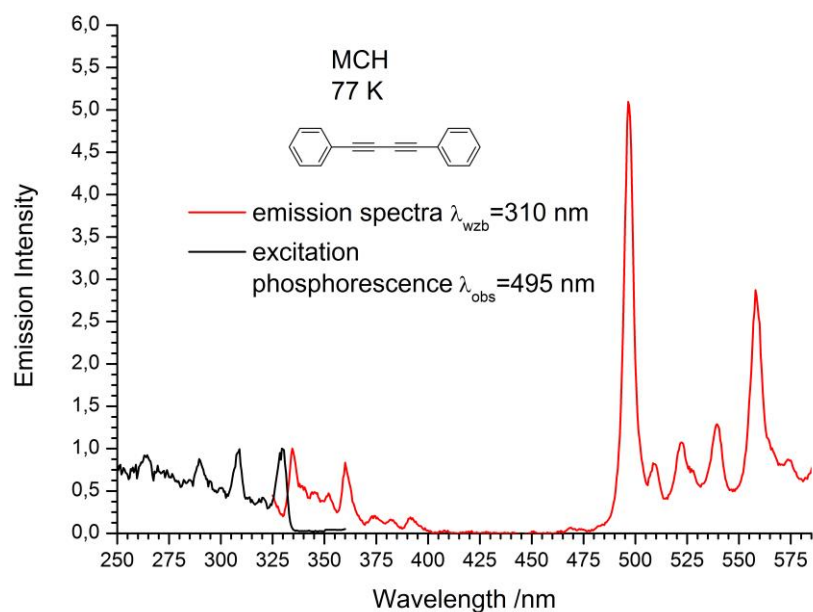


Fig. 11 ESI Luminescence and phosphorescence excitation spectra of DPB in methylcyclohexane at 77K.

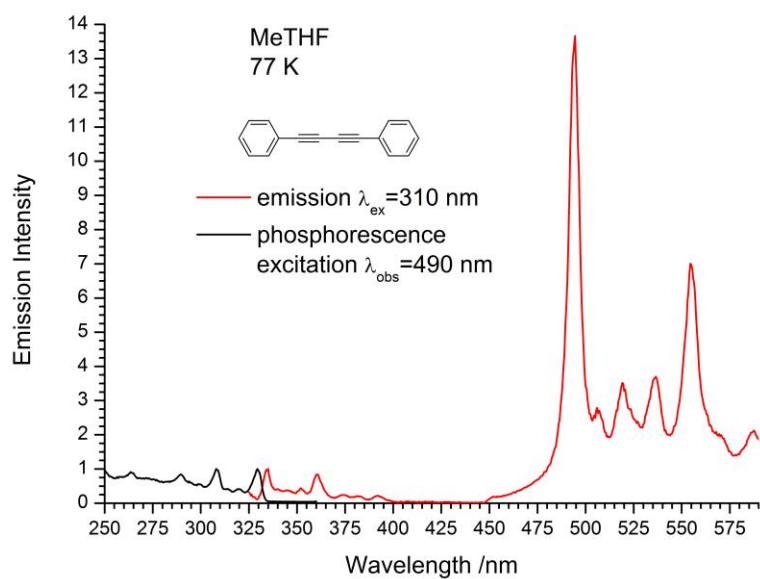


Fig. 12 ESI Luminescence and phosphorescence excitation spectra of DPB in 2-methyltetrahydrofuran at 77K.

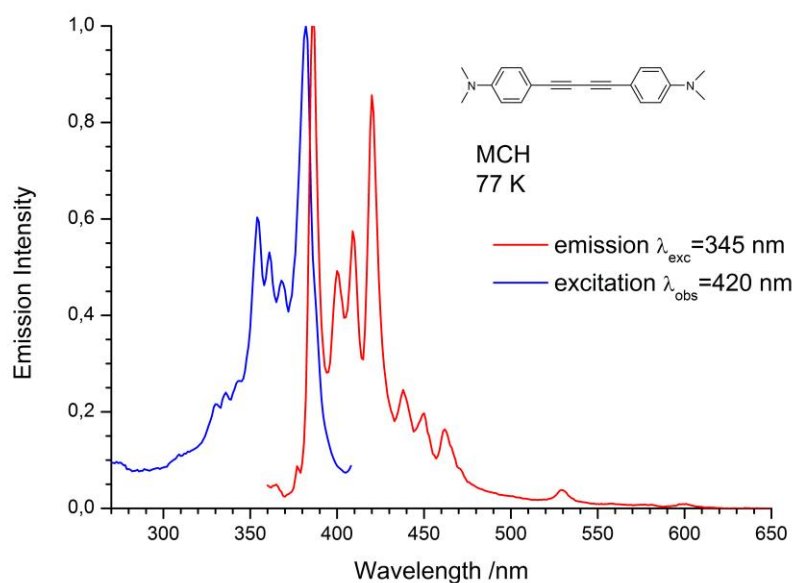


Fig. 13 ESI Luminescence and fluorescence excitation spectra of (DMAPh)₂DA in methylcyclohexane at 77K.

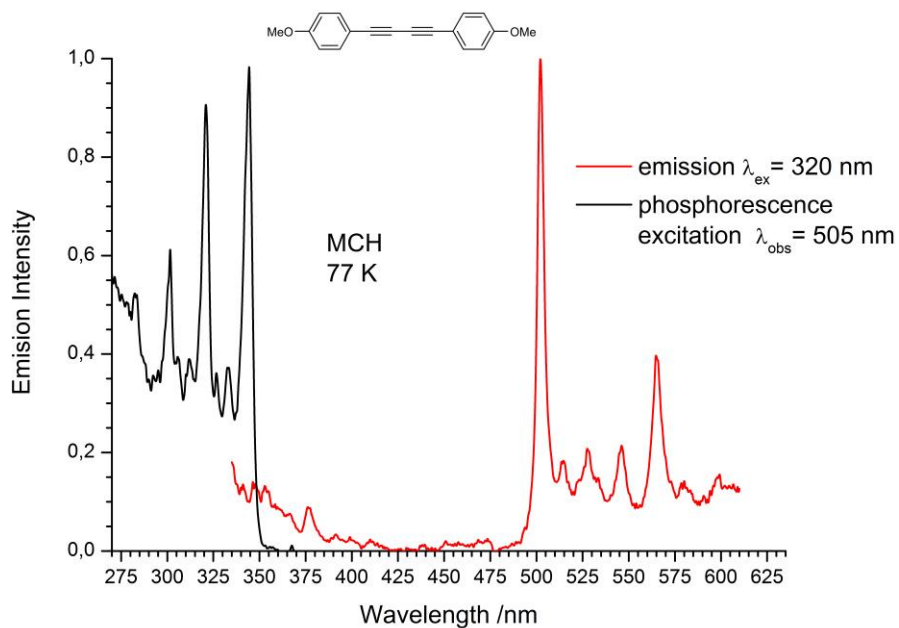


Fig. 14 ESI Luminescence and phosphorescence excitation spectra of $(\text{CH}_3\text{OPh})_2\text{DA}$ in methylcyclohexane at 77K.

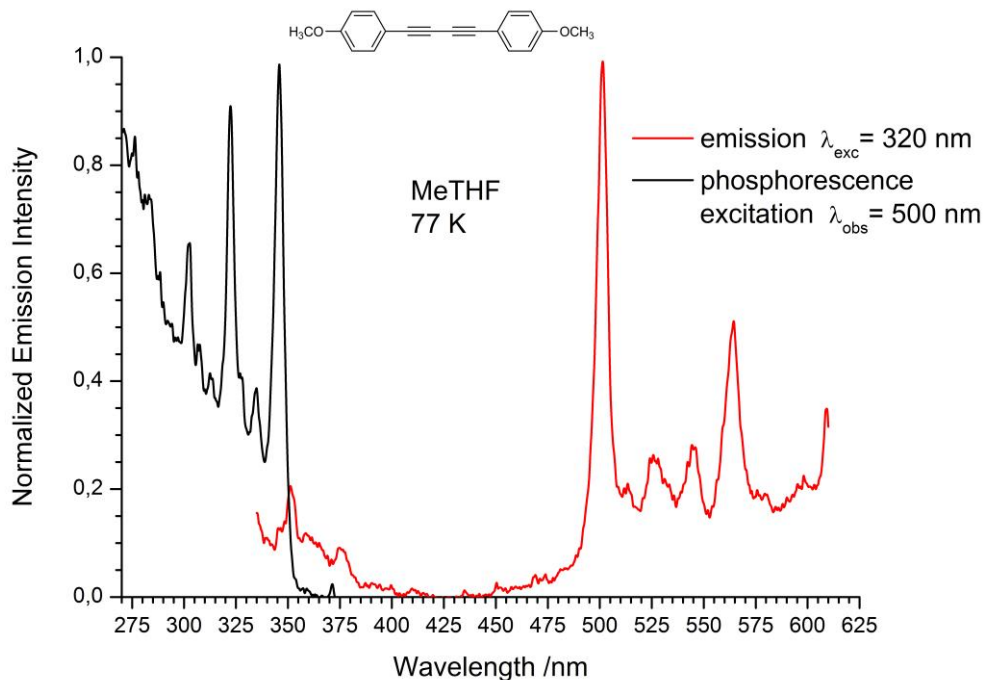


Fig. 15 ESI Luminescence and phosphorescence excitation spectra of $(\text{CH}_3\text{OPh})_2\text{DA}$ in 2-methyltetrahydrofuran at 77K.

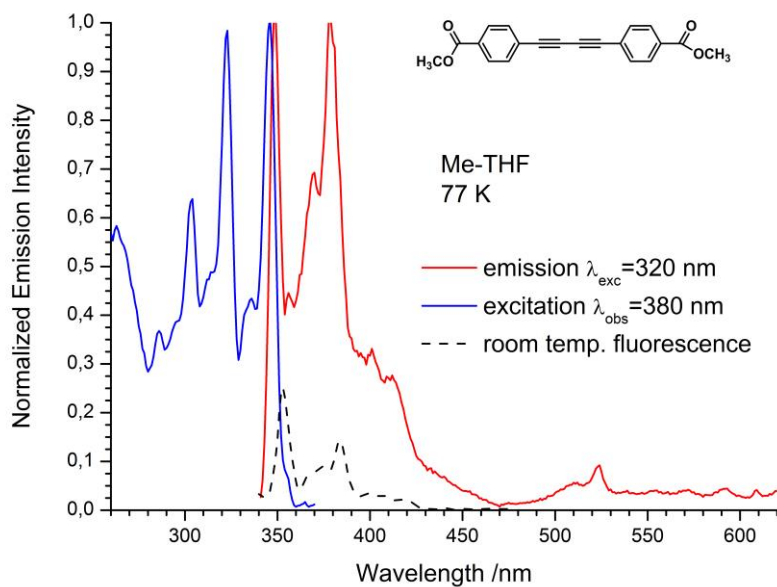


Fig. 16 ESI Luminescence and fluorescence excitation measured at 77K and room temperature fluorescence spectra of $(\text{CH}_3\text{O}_2\text{CPh})_2\text{DA}$ in 2-methyltetrahydrofuran.

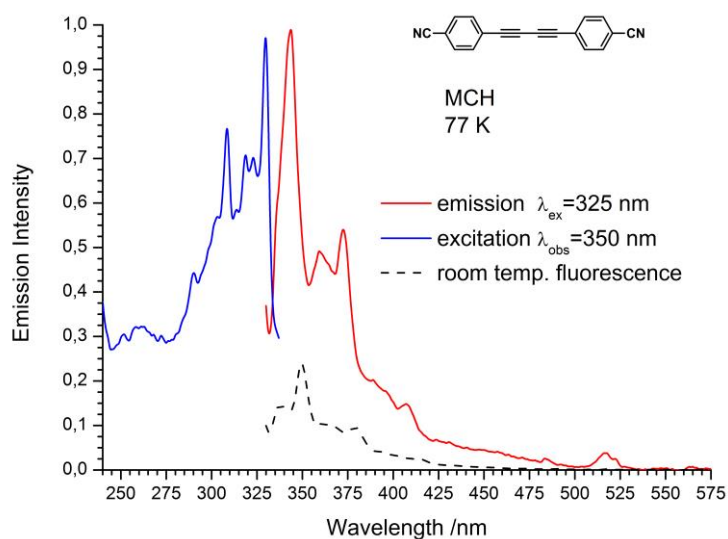


Fig. 17 ESI Luminescence and fluorescence excitation spectra measured at 77K and room temperature fluorescence spectra of $(\text{NCPH})_2\text{DA}$ in methylcyclohexane.

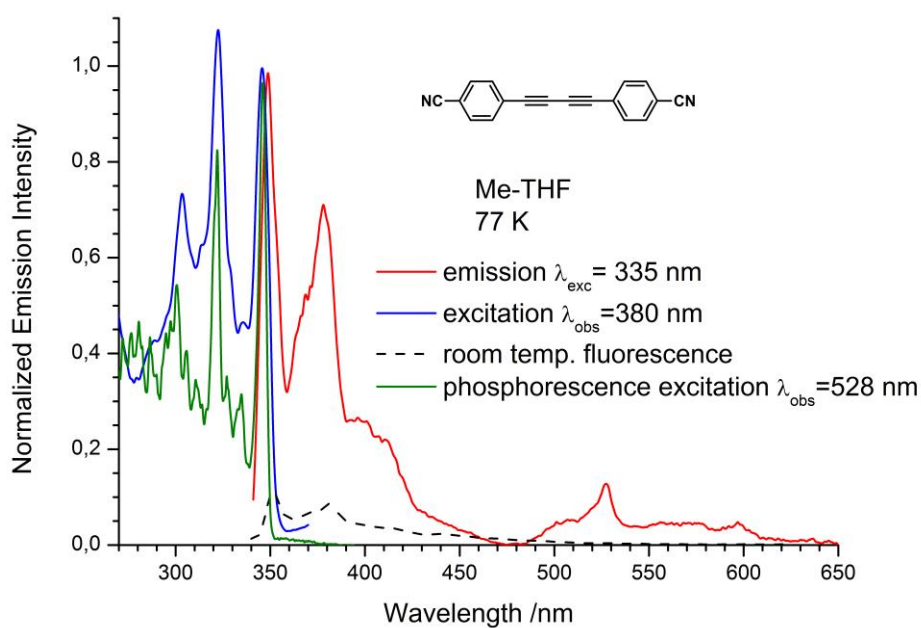


Fig. 18 ESI Luminescence (red line) and fluorescence (blue line) and phosphorescence (olive line) excitation and room temperature fluorescence spectra (dashed line) of $(\text{NCPH})_2\text{DA}$ in 2-methyltetrahydrofuran.

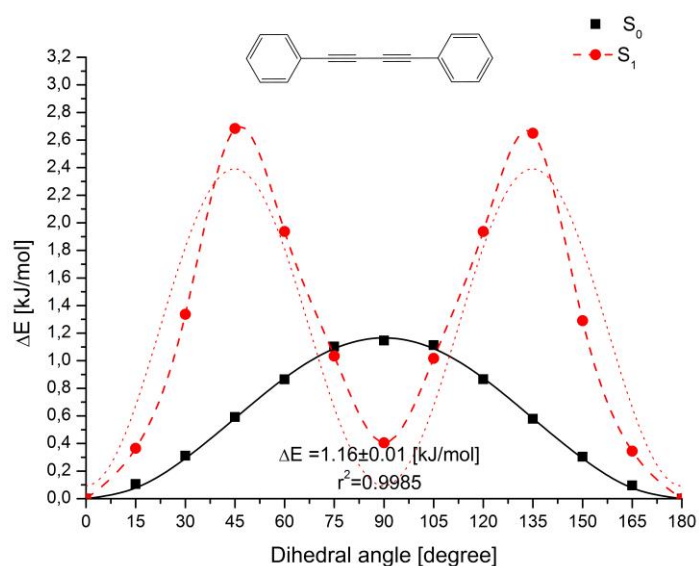


Fig. 19 ESI Torsional potentials of the S_0 (black solid line) and S_1 (red dashed line) states calculated for DPB. Red dotted line is represents best fit to the trigonometric

function given by eq. 2. Each energy was calculated at the optimized geometry of the respective electronic (S_0 or S_1) state for a given phenyl-phenyl torsional angle.

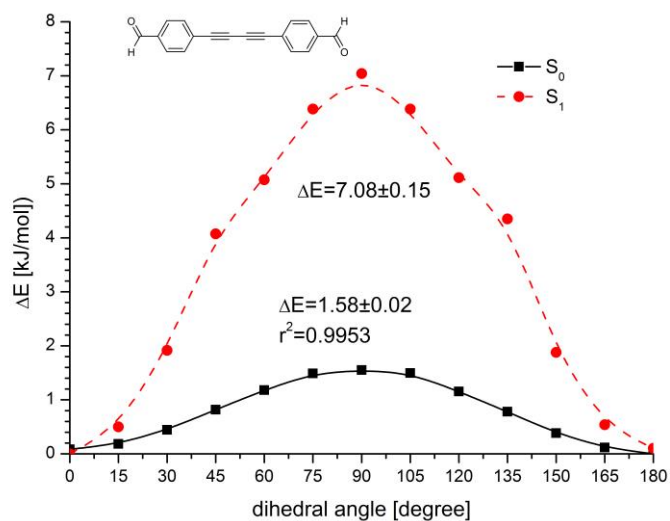


Fig. 20 ESI Torsional potentials of the S_0 (black solid line) and S_1 (red dashed line) states calculated for (OHCPH)₂DA. Each energy was calculated at the optimized geometry of the respective electronic (S_0 or S_1) state for a given phenyl-phenyl torsional angle.

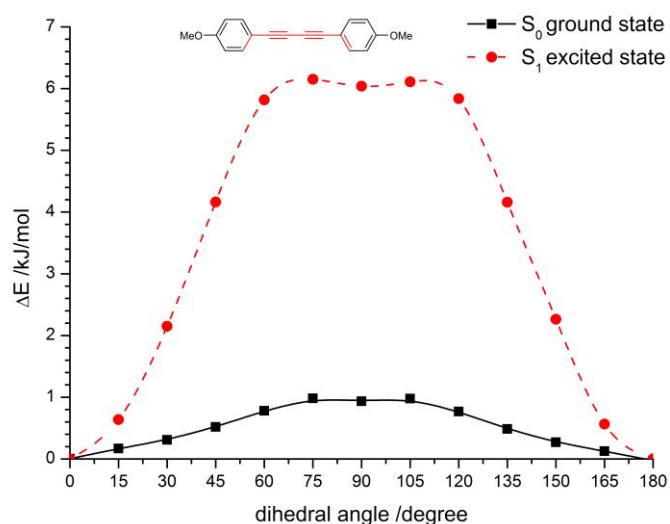


Fig. 21 ESI Torsional potentials of the S_0 (black solid line) and S_1 (red dashed line) states calculated for (CH₃OPh)₂DA. Each energy was calculated at the optimized

geometry of the respective electronic (S_0 or S_1) state for a given phenyl-phenyl torsional angle.

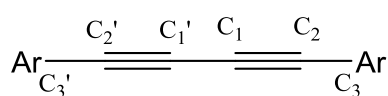
Table 3 ESI The energy of rotation barrier of diphenylbuta-1,3-diyne derivatives in the ground and excited state.

Substituent	ΔE (S_0) kJ/mol	ΔE (S_1) kJ/mol
-H	1.2	2.7
-OMe	1.0	6.2
-N(CH ₃) ₂	0.9	6.5
-COOCH ₃	1.5	6.0
-CN	1.5	5.5
-CHO	1.6	7.1

Table 4 ESI Bond length of buta-1,3-diyne unit* obtained from crystal structure and theoretical calculation for the ground (S₀) and excited (S₁) states.

compound	Bond of buta-1,3-diyne unit					state
	C _{3'} -C _{2'}	C _{2'} -C _{1'}	C _{1'} -C ₁	C ₁ -C ₂	C ₂ -C ₃	
DPB	1.432	1.194	1.372	1.195	1.433	cryst.
	1.418	1.214	1.356	1.214	1.418	S ₀
	1.382	1.254	1.310	1.254	1.382	S ₁
dDMADPB	1.425	1.208	1.368	1.208	1.425	cryst.
	1.416	1.216	1.356	1.216	1.416	S ₀
	1.380	1.248	1.318	1.248	1.380	S ₁
dOMeDPB	1.371	1.184	1.372	1.184	1.420	cryst.
	1.417	1.215	1.356	1.215	1.417	S ₀
	1.380	1.252	1.313	1.252	1.380	S ₁
dCOOMeDPB	1.432	1.205	1.371	1.204	1.433	cryst. ¹
	1.417	1.214	1.355	1.214	1.417	S ₀
	1.381	1.247	1.315	1.247	1.382	S ₁
dCHODPB	1.416	1.214	1.354	1.214	1.416	S ₀
	1.383	1.245	1.317	1.245	1.384	S ₁
	1.416	1.214	1.354	1.241	1.416	S ₀
dCNDPB	1.381	1.247	1.315	1.247	1.381	S ₁

1. T.M.Fasina, J.C.Collings, J.M.Burke, A.S.Batsanov, R.M.Ward, D.Albesa-Jove, L.Porres, A.Beeby, J.A.K.Howard, A.J.Scott, W.Clegg, S.W.Watt, C.Viney, T.B.Marder, *J.Mater.Chem.*, 2005 ,**15**, 690



bond numbering of buta-1,3-diyne unit

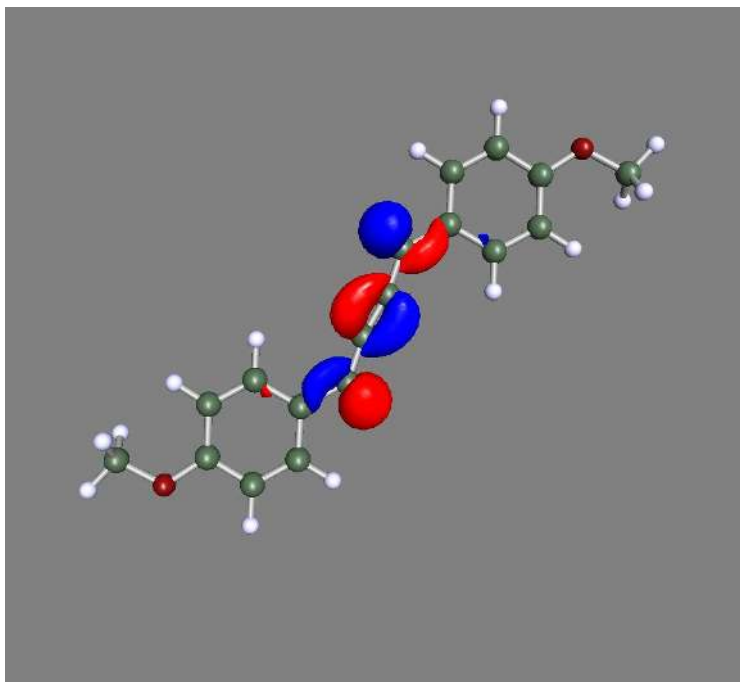


Fig 22 ESI The equilibrium optimized structure of $(\text{CH}_3\text{OPh})_2\text{DA}$ in the $\sigma\pi^*$ state and LUMO orbital.

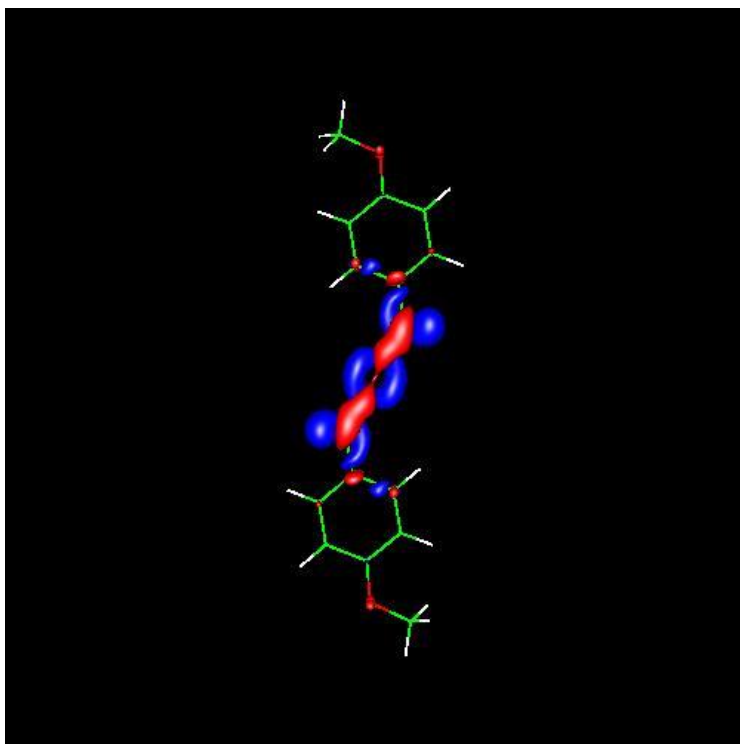


Fig 23 ESI The difference in electron density between ground and excited state of $(\text{CH}_3\text{OPh})_2\text{DA}$ in the $\sigma\pi^*$ state.

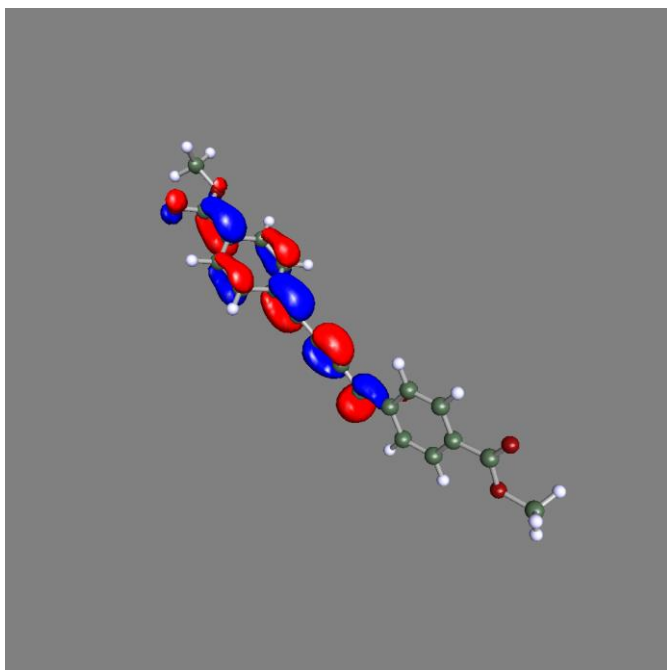


Fig. 24 ESI The optimized "scorpion like" structure of (CH₃O₂CPh)₂DA in the $\pi\pi^*$ state and LUMO orbital.

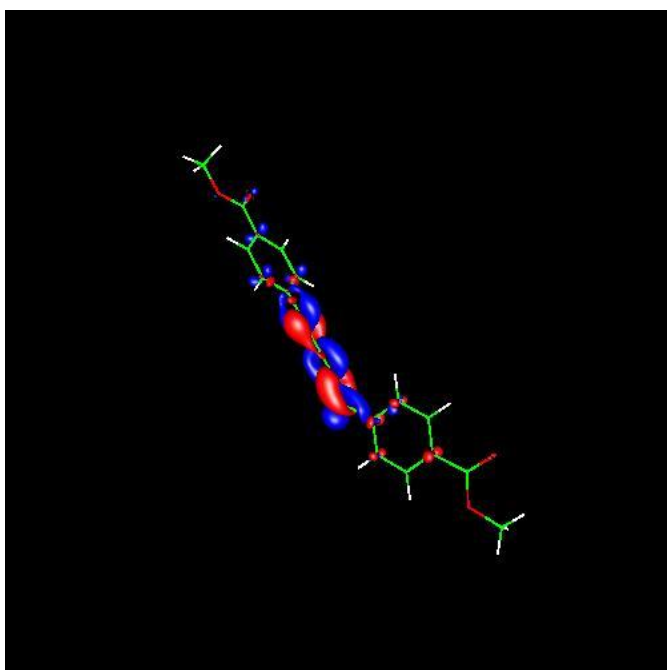


Fig 25 ESI The difference in electron density between ground and excited state of (CH₃O₂CPh)₂DA for "scorpion like" structure in $\pi\pi^*$ state.