Electronic Supplementary Material (ESI) for RSC Advances.

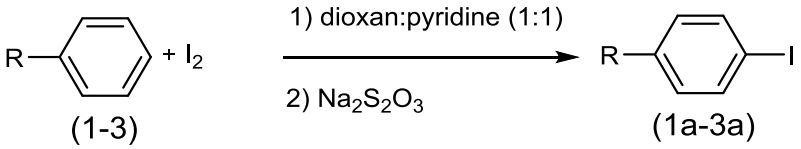
Electronic Supporting Informations

Experimental and theoretical studies of spectroscopic properties of the simple symmetrically substituted diphenylacetylene derivatives.

Małgorzata Wierzbicka, Irena Bylińska, Cezary Czaplewski, Wiesław Wiczk*

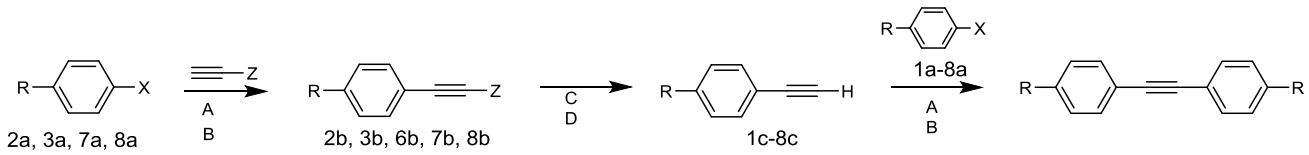
Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63,

80-952 Gdańsk, Poland



-N(Me)$_2$ (1)
-N(Bu)$_2$ (2)
-N(Hex)$_2$ (3)

Scheme 1 ESI Synthesis of 4-jodo N,N-alkylaminophenyl.



A: TEA, CuI, Pd[(Ph)$_3$P]$_2$Cl$_2$, T= 0^{o}C (for 1d-3d; 7-8b; 7-8d)
B: DMF, CuI, Pd(PPh$_3$)$_4$, TEA, T= 55^{o}C, Ar (for 2b-3b; 4d-5d, 6d)
C: Toluene, KOH, T= 80^{o}C, Ar (for 2c-3c; 8c)
D: DMF, KF, T=20^{o}C (for 6c-7c)

-R	**-X**	**-Z**	
-N(Me)$_2$ (1)	I	-	dDMADPA
-N(Bu)$_2$ (2)		-C(CH$_3$)$_2$OH	dDBADPA
-N(Hex)$_2$ (3)			dDHADPA
-OMe (4)		-	dOMeDPA
-H (5)			DPA
-CHO (6)	Br	-TMS	dCHODPA
-COOMe (7)	I	TMS	dCOOMeDPA
-CN (8)		-C(CH$_3$)$_2$OH	dCNDPA

Scheme 2 ESI Synthesis of symmetrically substituted diphenylacetylene and their precursors.

I. Synthesis of 4-iodo-N,N-dialkylaniline (1a-3a)

Compounds (1a-3a) were synthesized according to procedure described in literature[46].

Appropriate N,N-dialkylaniline (1-3) (1eq) was dissolved in dioxane/pyridine mixture (v/v 1/1) and the solution was cooled to 0^{o}C. Iodine (3eq) was added. After 1,5 h the ice bath was removed and next portion of iodine (1eq) was added. The reaction mixture was stirred for one

day. After the completion of reaction saturated solution of sodium thiosulfate was added. The reaction mixture was extracted into dichloromethane and washed with water. Combined organic layers were dried over anhydrous magnesium sulfate, filtered and the solvents were evaporated. The pure 1a-3a were obtained (Scheme 1 ESI).

General scheme for the synthesis of acetylene derivatives is shown in Scheme 2 ESI. Protected acetylene derivatives (2b, 3b, 7b, 8b) and symmetrically substituted acetylene derivatives (4,4'-(ethyne-1,2-diyl)bis(N,N-dimethylaniline) (dDMADPA), 4,4'-(ethyne-1,2-diyl)bis(N,N-dibutylaniline) (dDBADPA), 4,4'-(ethyne-1,2-diyl)bis(N,N-dihexylaniline) (dDHADPA), 1,2-bis(4-methoxyphenyl)ethyne (dOMeDPA), DPA, 4,4'-(ethyne-1,2-diyl)dibenzaldehyde (dCHODPA), dimethyl 4,4'-(ethyne-1,2-diyl)dibenzoate (dCOOMeDPA), 4,4'-(ethyne-1,2-diyl)dibenzonitrile (dCNDPA)) were prepared based on Sonogashira method[47,48] - coupling respective halogenoarenes with appropriate terminal ethynyl derivatives (procedure A or B, Scheme 2 ESI).

II. Synthesis of protected acetylene derivatives (7b, 8b) and symmetrical acetylene derivatives (dDMADPA, dDBADPA, dDHADPA, dCOOMeDPA, dCNDPA) (procedure A).

Appropriate halogenoarene (1 eq) was dissolved in triethylamine (TEA) and the solution was cooled to 0°C. Then trace amount copper iodide (CuI) and bis(triphenylphosphine)palladium (II) dichloride ($Pd[(Ph)_3P]_2Cl_2$) as catalysts were added. After a few minutes appropriate terminal acetylene derivatives (Scheme 2 ESI) (1.2 eq) were added. The reaction mixture was stirred for 12 h in temperature 0°C and if need for 24 h in temperature room. After completion of reaction, mixture was filtered and extracted into ethyl acetate. Organic layer was washed with water. Combined organic layers were dried over anhydrous magnesium sulfate, filtered and

the solvent was evaporated. The pure products were isolated by crystallization with mixture of ethyl acetate and petroleum ether (dCNDPA) or by column chromatography on silica gel (petroleum ether/ethyl acetate 7:1 v/v (7b); 10:1 v/v (8b, dCOOMeDPA); 15:1 v/v (dDBADPA, dDHADPA); 20:1 v/v (dDMADPA).

Synthesis of protected acetylene derivatives (2b-3b) and symmetrical acetylene derivatives (dOMeDPA, DPA, dCHODPA**)** (procedure B).

Stirred solution of appropriate halogenoarene (1 eq in case of iodo and 0.5 eq for bromo derivatives) in DMF with addition of TEA was degassed and trace amount of tetrakis(triphenylphosphine)palladium(0) and copper iodide as the catalysts were added. After few minutes appropriate terminal acetylene derivative (Scheme 2, ESI) (1 eq) was added. The reaction mixtures were stirred at about 55°C for couple of days. After the reaction was completed the crude products were filtered, extracted into toluene and washed with water, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated under reduced pressure. The pure products were isolated: by means of semi-preparative RP-HPLC (dOMeDPA, DPA) and by column chromatography on silica gel (petroleum ether/ethyl acetate 5:1 v/v (2b-3b); 10:1 v/v (dCHODPA)).

General procedure for removing of protecting group of acetylene derivatives is shown in Scheme 2 ESI. The removing of trimetylsilane group (TMS) (6c-7c) was made as described in literature[49] (procedure C) and removing of 2-hydroxy-2-methylpropyl group (2c-3c, 8c) as described in literature[50,51] (procedure D) (Scheme 2 ESI).

III. Removing the protective group (6c-7c) (procedure C)

Appropriate ethynyl derivative protected by trimetylsilane group (1eq) was dissolved in dimethylformamid (DMF) and potassium fluoride (3eq) was added. The reaction was stirred, under argon atmosphere, at temperature room for 1,5 h. Progress of reaction was monitored by TLC. After each reactions was completed, the reaction mixture was extracted into ethyl acetate and washed with water, dried over anhydrous magnesium sulfate, filtered and the solvents were evaporated under reduced pressure. The pure products 6c and 7c were isolated by multiple crystallization with mixture petroleum ether and ethyl acetate.

Removing the protective group (2c-3c, 8c) (procedure D)

A mixture of appropriate ethynyl derivative protected by 2-hydroxy-2-methylpropyl group (1eq) and potassium hydroxide (1eq) in toluene was heated under reflux for 2 h under argon atmosphere. Progress of reaction was monitored by TLC. After the reaction was completed, the reaction mixture was cooled, filtered, extracted into ethyl acetate and washed with 0.1 M solution of $KHSO_4$ and with water. Combined organic layers were dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated under reduced pressure. The pure products were isolated by column chromatography on silica gel (petroleum ether/ethyl 5:1 v/v (2c-3c) or by multiple crystallization with mixture petroleum ether and ethyl acetate (8c).

Identification data of synthesized compounds.

4,4'-(ethyne-1,2-diyl)bis(N,N-dimethylaniline) (dDMADPA) (yield 31,6%)

1H-NMR (500 MHz, CDCl3), δ (ppm): 3,00 (s, 12H, 4(CH3)); 6,65 (d, 4H, C3H, C7H, C3'H, C7'H, J= 10 Hz); 7,41 (d, 4H, C4H, C6H, C4'H, C6'H, J= 10 Hz)

13C-NMR (100 MHz, CDCl3), δ (ppm): 40,04 4(CH3); 82,13 C1, C1'; 108,74 C2, C2'; 111,84 C3, C7, C3', C7'; 133,79 C4, C6, C4', C6'; 150,36 C5, C5'

MS (m/z): 265 (M+H), Ramman ν: 2205 cm-1 C≡C

4,4'-(ethyne-1,2-diyl)bis(N,N-dibutylaniline) (dDBADPA) (yellow oil; yield 35%)

1H-NMR (500 MHz, CDCl3), δ (ppm): 0.93-0.96 (t, 12H, C12'H, C16'H, C12H, C16H); 1.19-1.38 (m, 8H, C11'H, C15'H, C11H, C15H); 1.50-1.57 (m, 8H, C10'H, C14'H, C10H, C14H); 3.20-3.24 (t, 8H, C9'H, C13'H, C9H, C13H); 6.40-6.42 (d, 4H, C6'H, C4'H, C6H, C4H, J=10 Hz); 7.39-7.42 (d, 4H, C3'H, C7'H, C3H, C7H, J=15 Hz).

MS (m/z): 432, 433 (M+, $M+H^+$), Ramman ν: 2172 cm-1

4,4'-(ethyne-1,2-diyl)bis(N,N-dihexylaniline) (dDHADPA) (yellow oil; yield 15%)

1H-NMR (500 MHz, CDCl3), δ (ppm): 0.88-0.91 (t, 12H, C14'H, C20'H, C14H, C20H); 1.26-1.30 (m, 24H, C11'H-C13'H, C17'H-C19'H, C11H-C13H, C17H-C19H); 1.52-1.60 (m, 8H, C10'H, C16'H, C10H, C16H); 3.18-3.22 (t, 8H, C9'H, C15'H, C9H, C15H); 6.39-6.41 (d, 4H, C6'H, C4'H, C6H, C4H, J=10 Hz); 7.39-7.42 (d, 4H, C3'H, C7'H, C3H, C7H, J=15 Hz).

MS (m/z): 545, 546 (M+, $M+H^+$), Ramman ν: 2183 cm-1

dimethyl 4,4'-(ethyne-1,2-diyl)dibenzoate (dCOOMeDPA) (yield 56%)

1H-NMR (500 MHz, CDCl3): δ (ppm): 3,96 (s, 6H, 2(OCH3), 7,63 (d, 4H, C3H, C7H, C3'H, C7'H, J=10 Hz); 8,065 (d, 4H, C4H, C6H, C4'H, C6'H, J=10 Hz)

13C-NMR (100 MHz, CDCl3) δ (ppm): 52,33 2(OCH3); 91,42 C1,C1', 127,35 C2, C2'; 129,67 C3, C7, C3',C7'; 130,0 C4, C6, C4',C6'; 131,65 C5, C5'; 166,51 C8, C8';

MS (m/z) : 294 (M), Ramman ν: 2243 cm-1 C≡C

4,4'-(ethyne-1,2-diyl)dibenzonitrile (dCNDPA) (yield 51,5 %)

1H-NMR (500 MHz, CDCl3): δ (ppm): 7, 65 (q, 8 H, C3H, C7H, C3'H, C7'H, C4H, C6H, C4'H, C6'H , J= 9,5 Hz, J= 14,5 Hz)

13C-NMR (100 MHz, CDCl3) δ (ppm): 91,52 C1, C1; 112,36 C5, C5'; 118,96; C8, C8'; 127,51 C2, C2'; 132,43 C4, C6, C4', C6'; 133,61 C3, C7, C3', C7';

MS (m/z): 228 (M), Ramman ν: 2227 cm-1 C≡C

4,4'-(ethyne-1,2-diyl)dibenzaldehyde (dCHODPA) (yield 53,3%)

1H-NMR (500 MHz, CDCl3): δH (ppm): 7,72 (d, 4H, C3H, C7H, C3’H, C7’H, J= 9,4 Hz); 7,91 (d, 4H, C4H, C6H, C4’H, C6’H, J= 9,4 Hz); 10,04 (s, 2 H, C8H, C8’H)

13C-NMR (100 MHz, CDCl3) δ (ppm): 92,31 C1, C1’; 128,89 C2, C2’; 129,82 C3, C7, C3’, C7’;132,53 C4, C6, C4’, C6’;136,16 C5, C5’; 191,44 C8, C8’;

MS (m/z) : 235 ($M+H^+$), Ramman ν: 2218 cm-1 C≡C

1,2-diphenylethyne (DPA) (yield 33,5 %)

1H-NMR (500 MHz, CDCl3): δ (ppm): 7,35-7,41 (m, 6H, C4H,C5H,C6H,C4’H,C5’H,C6’H); 7,54-7,59 (m, 4H, C3H, C7H, C3’H, C7’H);

13C-NMR (100 MHz, CDCl3): δ (ppm): 89,62 C1,C1’; 123,53 C2,C2’; 128,51 C5,C5’; 128,60 C4,C6,C4’,C6’; 131,87 C3,C7, C3’,C7’;

MS (m/z): 178 (M), Ramman ν: 2224 cm-1 C≡C

1,2-bis(4-methoxyphenyl)ethyne (dOMeDPA) (yield 51%)

1H-NMR (500 MHz, CDCl3): δ (ppm): 3,82 (s, 6H, 2(CH3); 6,87 (d, 4H, C4H, C6H, C4’H, C6’H, J=8,0 Hz); 7,45 (d, 4H, C3H, C7H, C3’H, C7’H, J=8,40 Hz);

13C-NMR (100 MHz, CDCl3) δ (ppm): 56,77 C1, C1’; 78,5 C2, C2’; 115,47 C4, C6, C4’,C6’; 134,36 C3, C7,C3’, C7’; 160,92 C5, C5’,

MS (m/z) :238 (M), Ramman ν: 2215,4 cm-1 C≡C

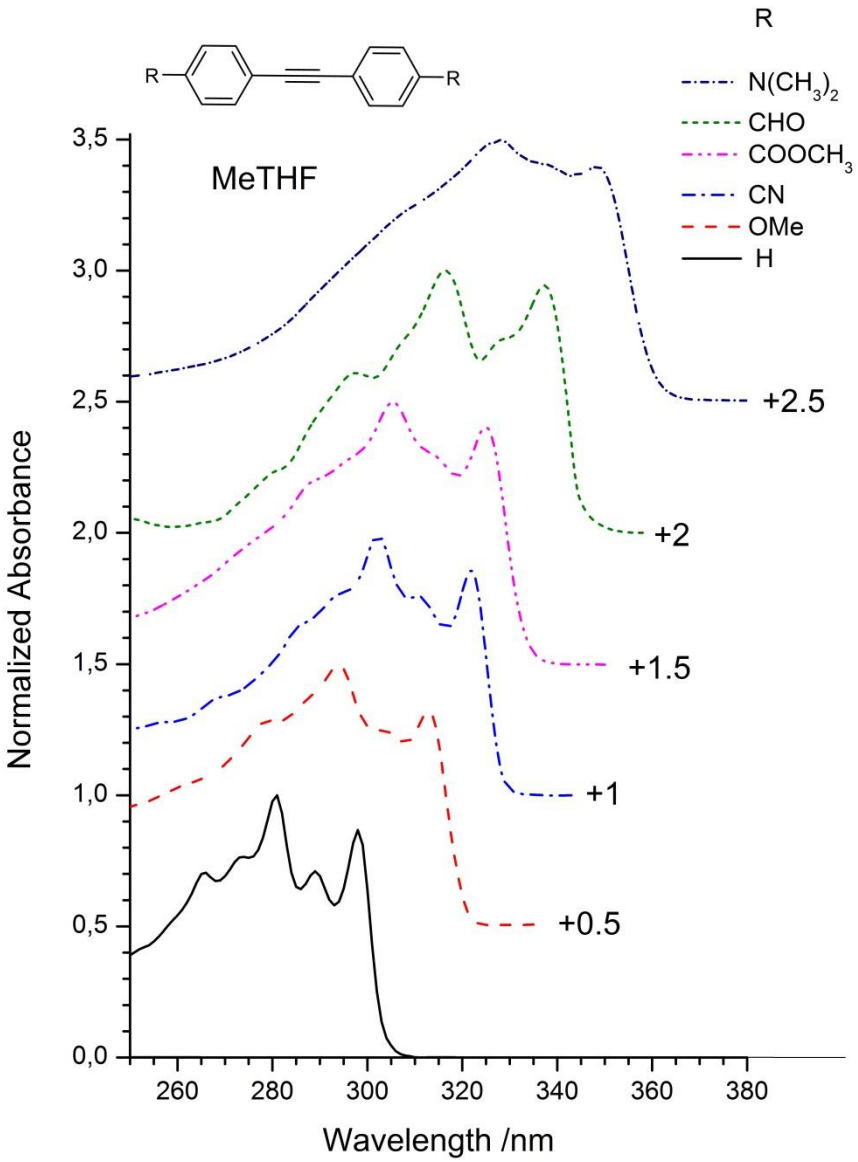


Fig. 1 ESI Absorption spectra of DPA and its derivatives in 2-methyltetrahydrofuran at room temperature.

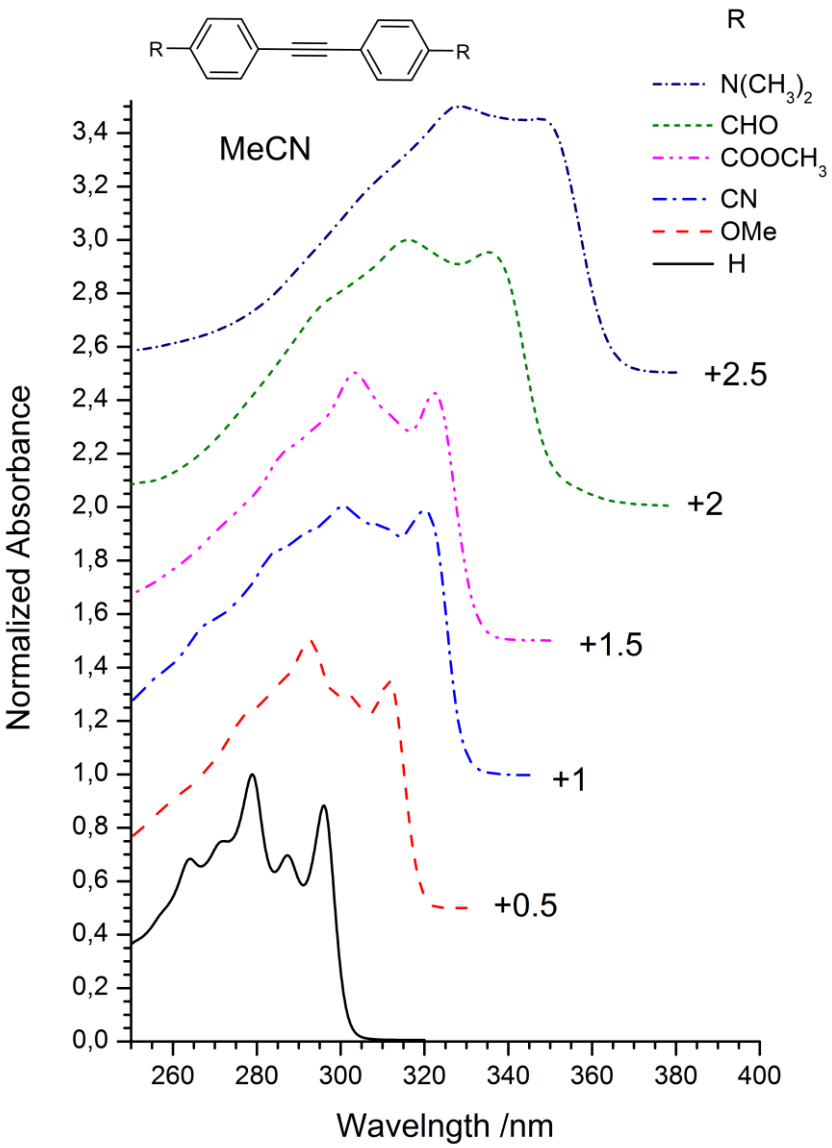


Fig. 2 ESI Absorption spectra of DPA and its derivatives in acetonitrile at room temperature.

Table 1 ESI The solvatochromic shift of absorption spectra of 4,4` substituted phenylacetylene.

Substituent	di-phenytlacetylene derivative		
	MeCx λ /nm	MeTHF λ /nm	MeCN λ /nm
-H	298	298	296
-OMe	312.5	312.5	311.5
-CN	321.5	321.5	320
-COOMe	325	324.5	322
-CHO	337	337	335.5
-DMA	345.5	348.5	348

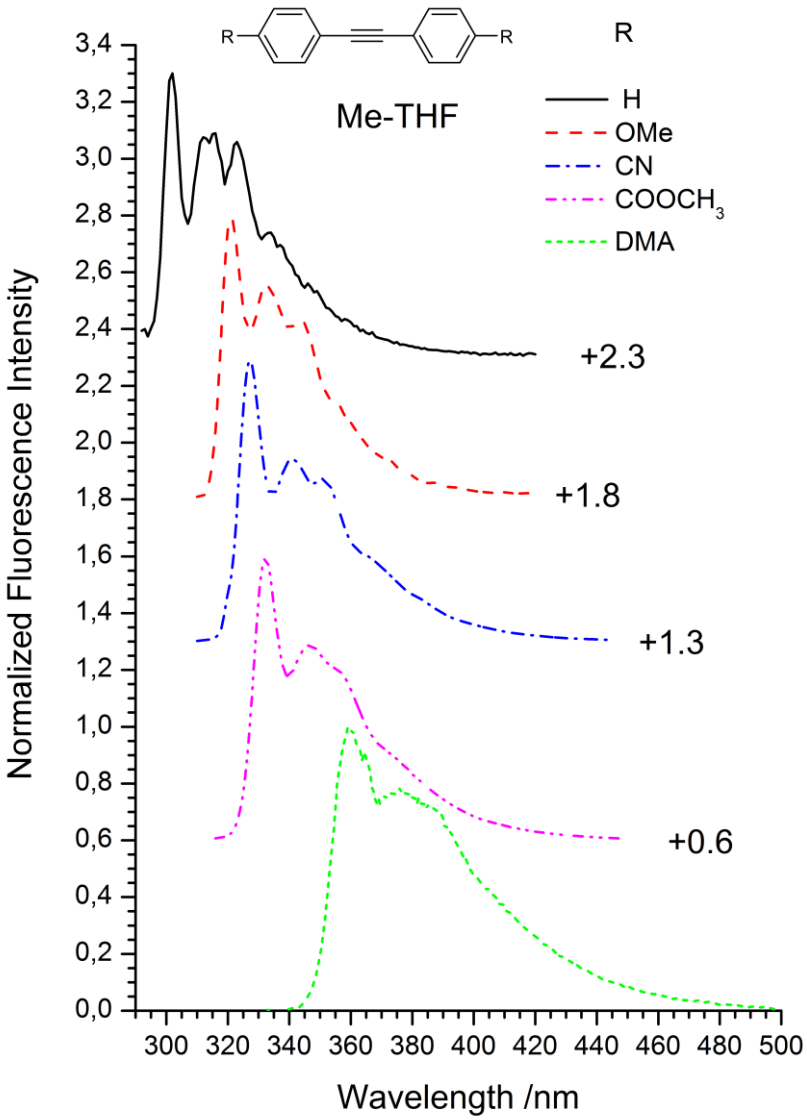


Fig. 3 ESI Fluorescence spectra of DPA and its derivatives in 2-methyltetrahydrofuran at room temperature.

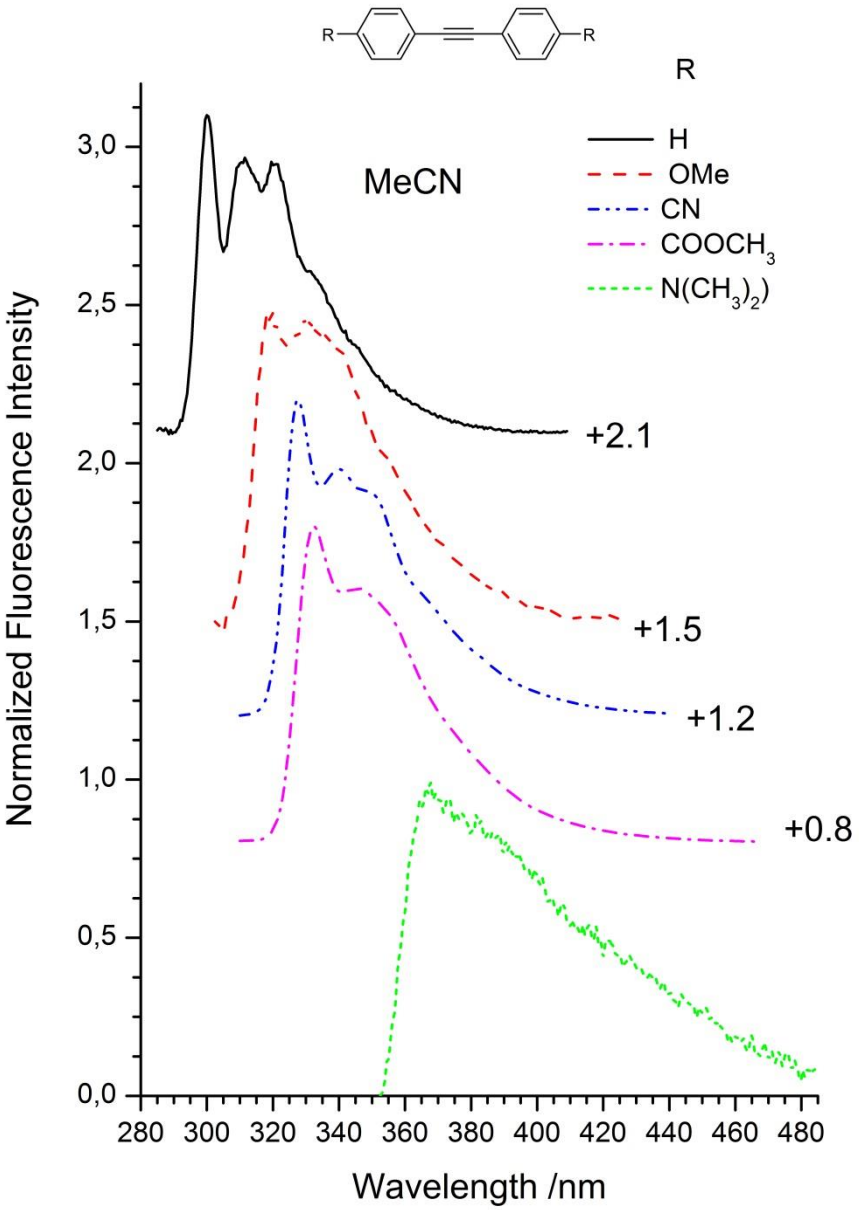


Fig. 4 ESI Fluorescence spectra of DPA and its derivatives in acetonitrile at room temperature.

Table 2 ESI The solvatochromic shift of fluorescence spectra of 4,4` substituted diphenylacetylene.

Substituent	phenytlacetylene derivative		
	MeCx λ /nm	MeTHF λ /nm	MeCN λ /nm
-H	302	301.5	300
-OMe	316.5	321	319
-CN	326.5	327	327.5
-COOMe	330	332.5	332.5
-DMA	351.5	359.5	367.5

Table 3 ESI Fluorescence quantum yield of diphenylacetylene and its derivatives in different solvents.

Compound	Solvent	φ
DPA	MeCN	0.008
	CX	0.005
	C_6H_{14}	0.008
	$C_{16}H_{34}$	0.007
	Me-CX	0.005
	Me-THF	0.004
dDMADPA	MeCN	0.004
	CX	0.061
	C_6H_{14}	0.048
	$C_{16}H_{34}$	0.046
	Me-CX	0.045
	Me-THF	0.040

dOMeDPA	MeCN	0.005
	CX	0.010
	C_6H_{14}	0.008
	$C_{16}H_{34}$	0.010
	Me-CX	0.011
	Me-THF	0.008
dCOOMeDPA	MeCN	0.27
	CX	0.30
	C_6H_{14}	0.31
	$C_{16}H_{34}$	0.34
	Me-CX	0.28
	Me-THF	0.25
dCNDPA	MeCN	0.28
	CX	0.34
	C_6H_{14}	0.33
	$C_{16}H_{34}$	0.38
	Me-CX	0.32
	Me-THF	0.30

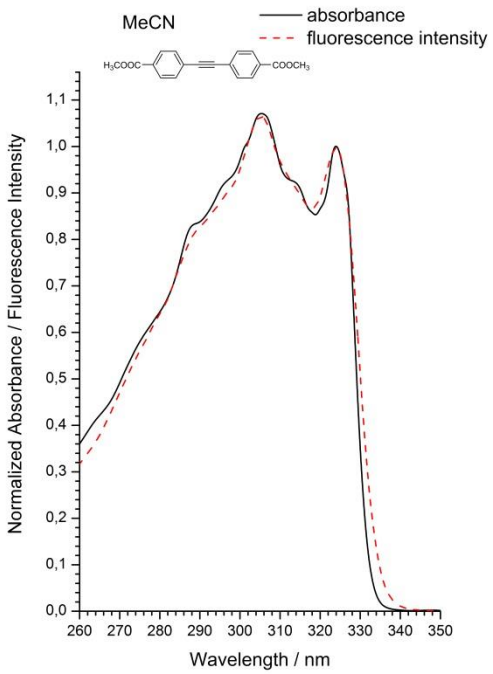


Fig. 5 ESI Absorption (solid line) and fluorescence excitation spectrum (dashed line) of dCOOMeDPA in acetonitrile.

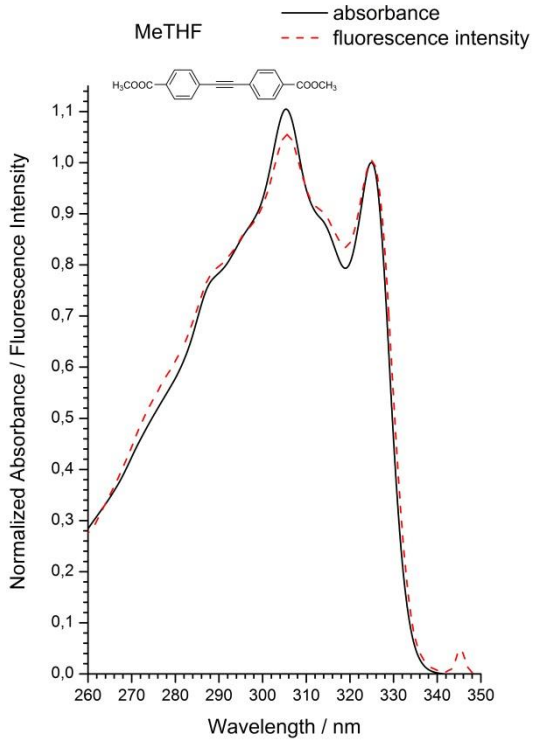


Fig. 6 ESI Absorption (solid line) and fluorescence excitation spectrum (dashed line) of dCOOMeDPA in 2-methyltetrahydrofuran.

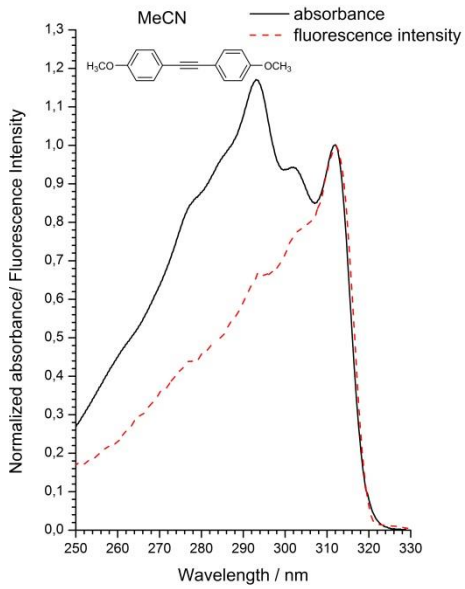


Fig. 7 ESI Absorption (solid line) and fluorescence excitation spectrum (dashed line) of dOMeDPA in acetonitrile.

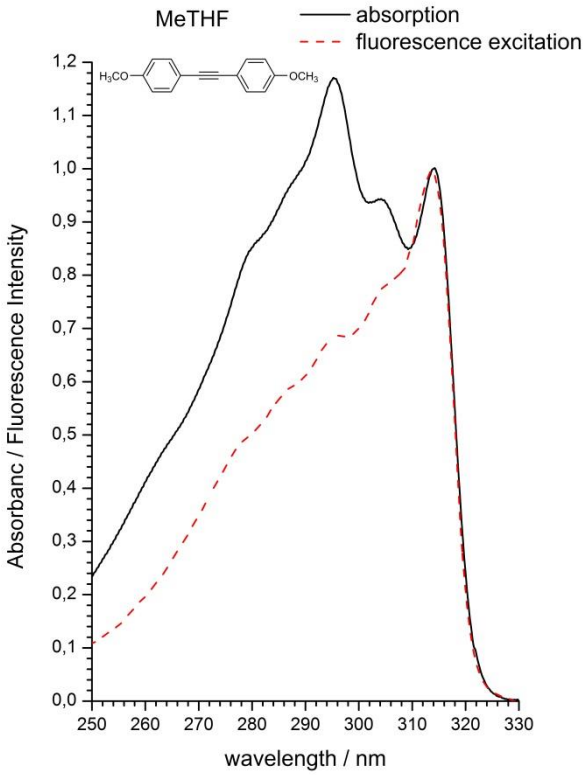


Fig. 8 ESI Absorption (solid line) and fluorescence excitation spectrum (dashed line) of dOMeDPA in 2-methyltetrahydrofuran.

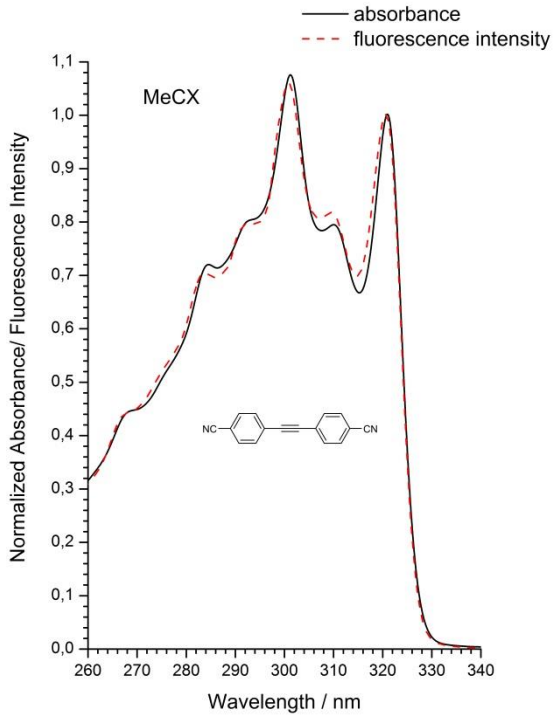


Fig. 9 ESI Absorption (solid line) and fluorescence excitation spectrum (dashed line) of dCNDPA in methylcyclohexane.

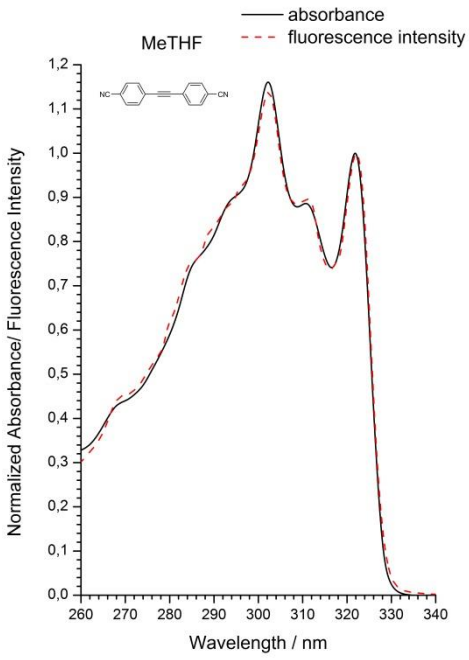


Fig. 10 ESI Absorption (solid line) and fluorescence excitation spectrum (dashed line) of dCNDPA in 2-methyltetrahydrofuran.

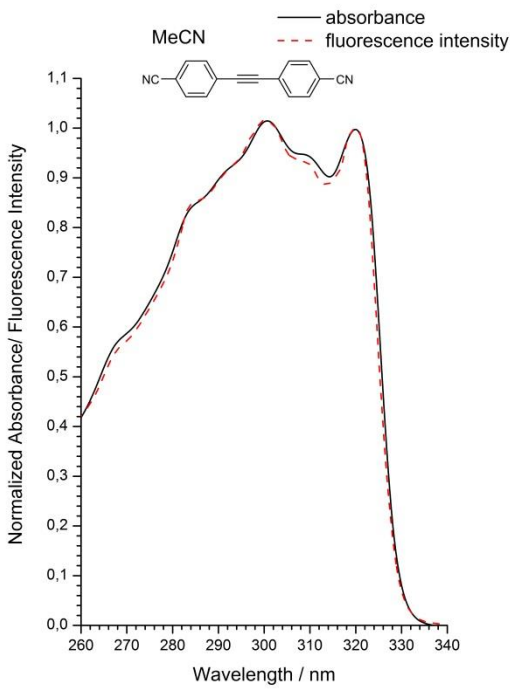


Fig. 11 ESI Absorption (solid line) and fluorescence excitation spectrum (dashed line) of dCNDPA in acetonitrile.

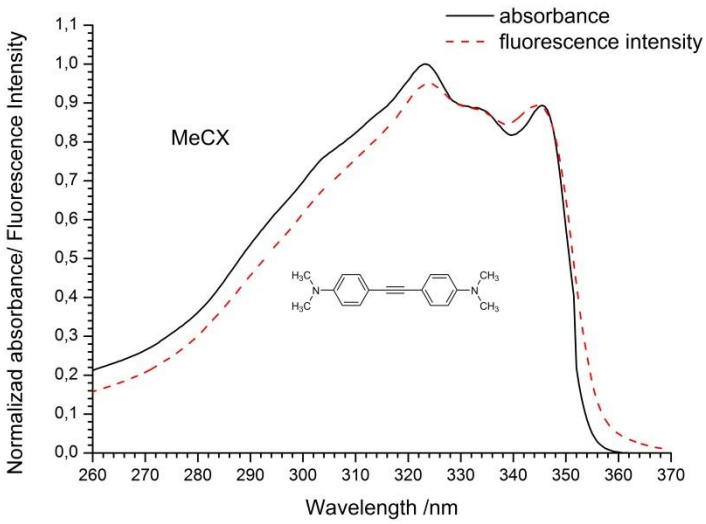


Fig. 12 ESI Absorption (solid line) and fluorescence excitation spectrum (dashed line) of dDMADPA in methylcyclohexane.

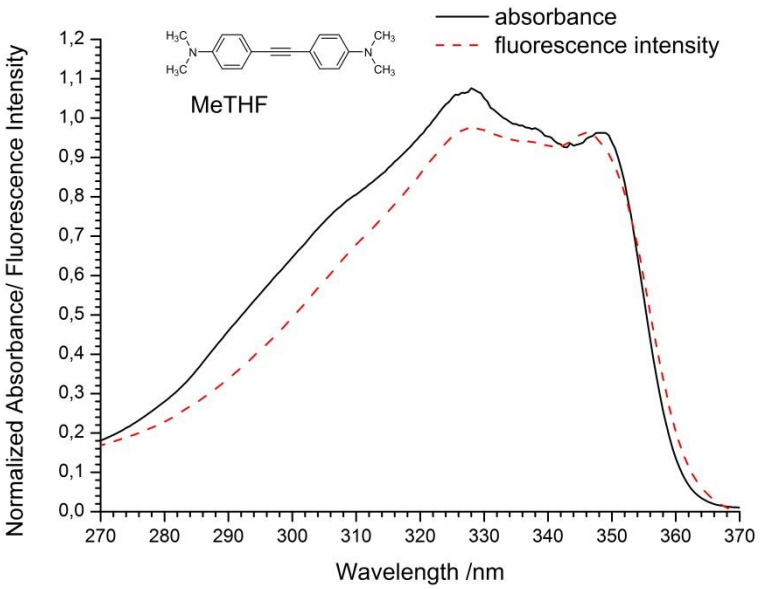


Fig. 13 ESI Absorption (solid line) and fluorescence excitation spectrum (dashed line) of dDMADPA in 2-methyltetrahydrofuran.

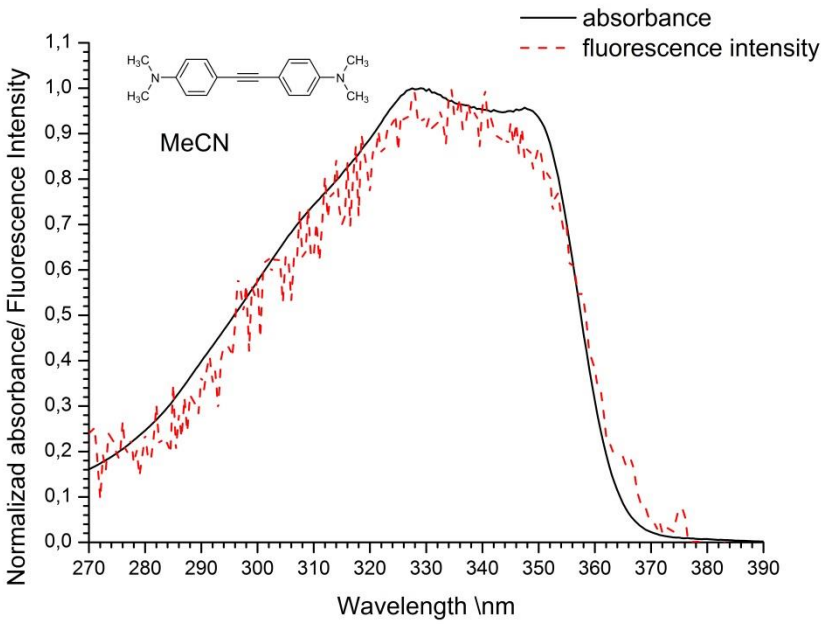
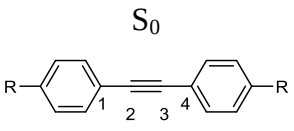
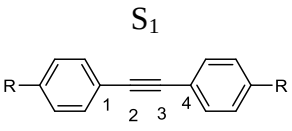
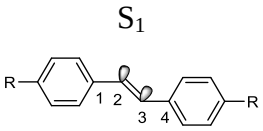
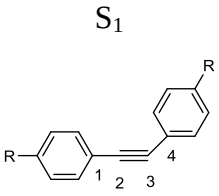


Fig. 14 ESI Absorption (solid line) and fluorescence excitation spectrum (dashed line) of dDMADPA in acetonitrile.

Table 4 ESI. Fluorescence lifetimes (τ), pre-exponential factors (α) and quality of the fit (χ_R^2) of dCOOMeDPA, dCNDPA and dDMADPA in selected solvents.

Compound	Solvent	τ(ns)	α	χ^2_R
dCOOMeDPA	MeCN	0.65	1	0.94
	CX	0.68	1	0.86
	C_6H_{14}	0.69	1	0.91
	$C_{16}H_{34}$	0.71	1	0.99
	MeCX	0.64	1	0.91
	MeTHF	0.64	1	0.90
dCNDPA	MeCN	0.67	1	0.88
	CX	0.68	1	0.90
	C_6H_{14}	0.69	1	0.82
	$C_{16}H_{34}$	0.70	1	0.97
	MeCX	0.67	1	0.95
	MeTHF	0.67	1	0.81
dDMADPA	MeCN	1.441	0.042	
		0.017	0.958	1.07
	CX	0.471	0.055	1.02
		0.071	0.945	
	C_6H_{14}	0.484	0.028	1.00
		0.057	0.972	
	$C_{16}H_{34}$	0.469	0.053	1.06
		0.069	0.947	
	MeCX	0.511	0.063	1.07
		0.069	0.937	
	MeTHF	0.895	0.033	1.06
		0.039	0.967	

Table 5 ESI Bond length of acetylenic unit of symmetrically substituted phenylacetylene derivatives in the ground state (S_0) and excited state (S_1) for a linear and bent structures.

compound	S_0 	S_1 	S_1 	S_1 

Bond lenght [Å]	**C_1 - C_2**	**C_2 – C_3**	**C_3 – C_4**	**C_1 - C_2**	**C_2 – C_3**	**C_3 – C_4**	**C_1 - C_2**	**C_2 – C_3**	**C_3 – C_4**	**C_1 - C_2**	**C_2 – C_3**	**C_3 – C_4**
dDMADPA	1.419	1.211	1.419	1.379	1.24	1.379	1.42	1.336	1.42	1.365	1.293	1.425
dOMeDPA	1.421	1.21	1.421	1.377	1.244	1.377	1.42	1.341	1.42	1.364	1.302	1.419
DPA	1.422	1.209	1.422	1.377	1.247	1.377	1.422	1.346	1.422	1.416	1.307	1.361
dCHODPA	1.419	1.209	1.419	1.382	1.238	1.382	1.421	1.348	1.421	-	-	-
dCOOMeDPA	1.420	1.209	1.420	1.380	1.240	1.380	1.421	1.347	1.421	1.360	1.291	1.408
dCNDPA	1.419	1.204	1.419	1.379	1.240	1.379	1.421	1.346	1.421	1.360	1.293	1.409

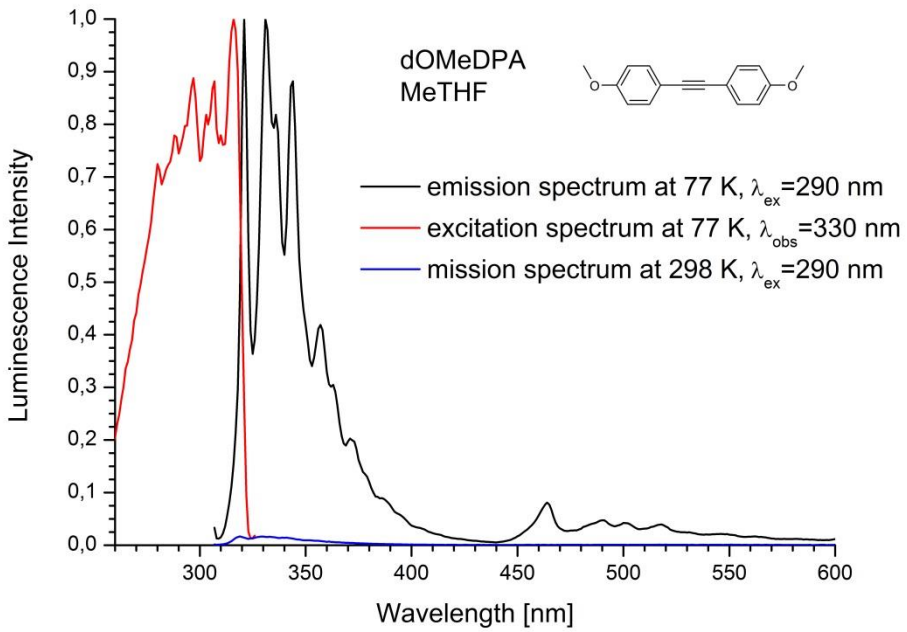


Fig. 15 ESI Luminescence (black line), fluorescence excitation spectrum (red line) measured at 77 K and fluorescence spectrum (blue line) measured at room temperature of dOMeDPA in 2-methyltetrahydrofuran.

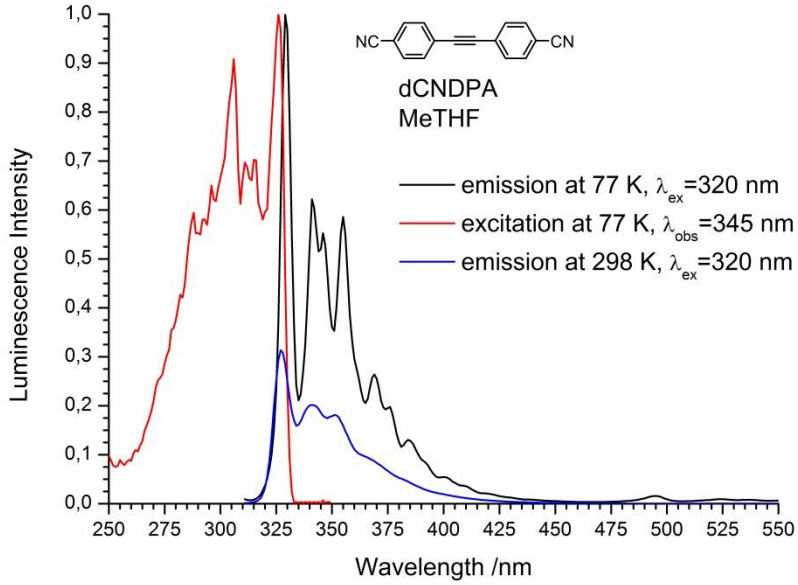


Fig. 16 ESI Luminescence (black line), fluorescence excitation spectrum (red line) measured at 77 K and fluorescence spectrum (blue line) measured at room temperature of dCNDPA in 2-methyltetrahydrofuran.

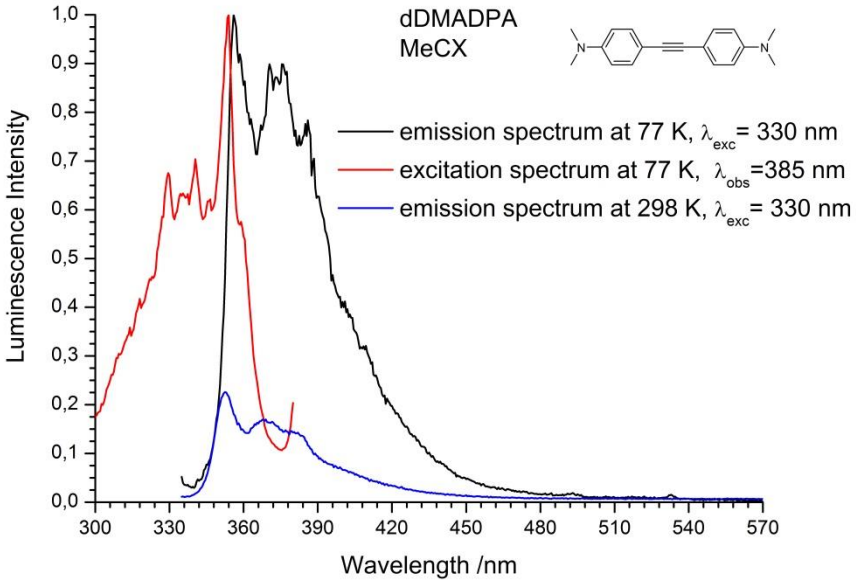


Fig. 17 ESI Luminescence (black line), fluorescence excitation spectrum (red line) measured at 77 K and fluorescence spectrum (blue line) measured at room temperature of dDMADPA in methylcyclohexane.

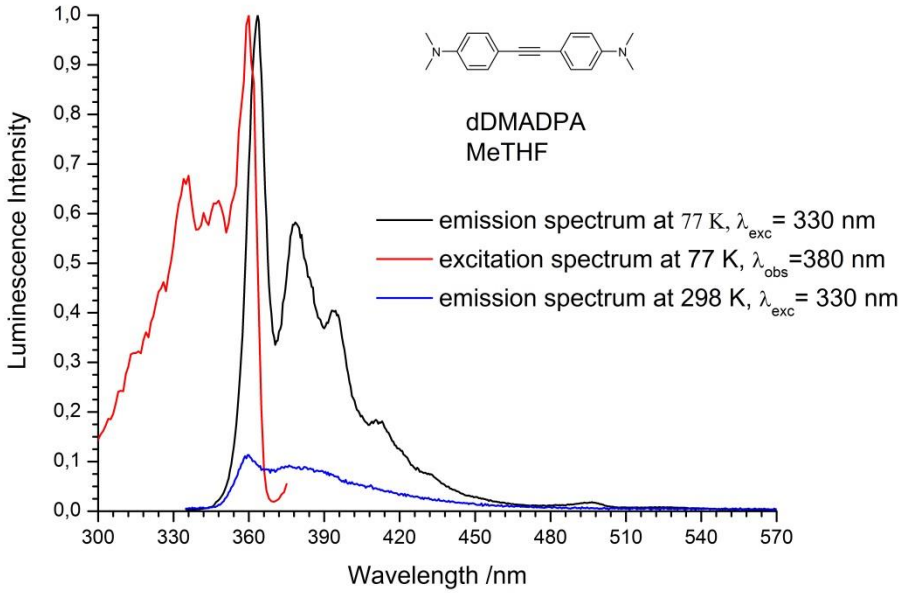


Fig. 18 ESI Luminescence (black line), fluorescence excitation spectrum (red line) measured at 77 K and fluorescence spectrum (blue line) measured at room temperature of dDMADPA in 2-methyltetrahydofuran.

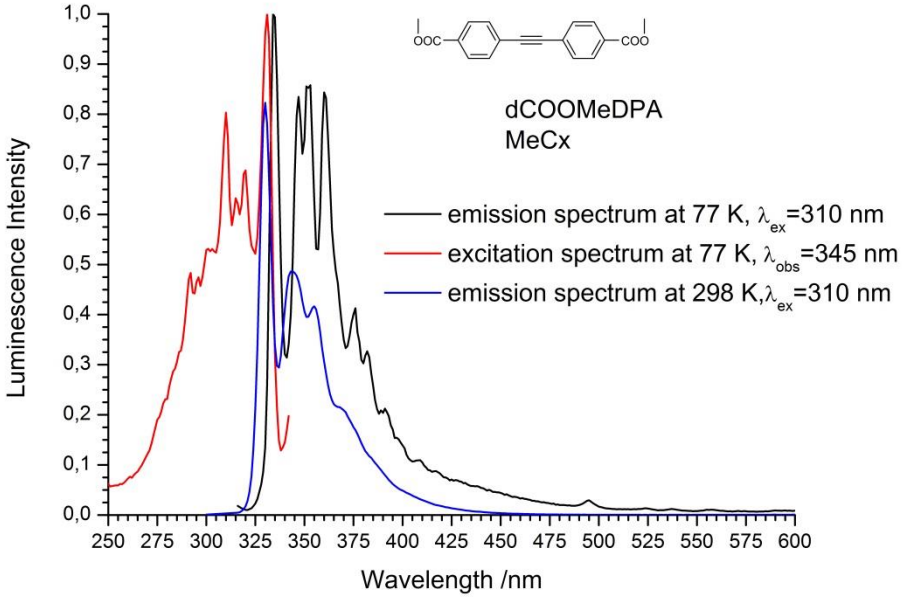


Fig. 19 ESI Luminescence (black line), fluorescence excitation spectrum (red line) measured at 77 K and fluorescence spectrum (blue line) measured at room temperature of dCOOMeDPA in methylcyclohexane.

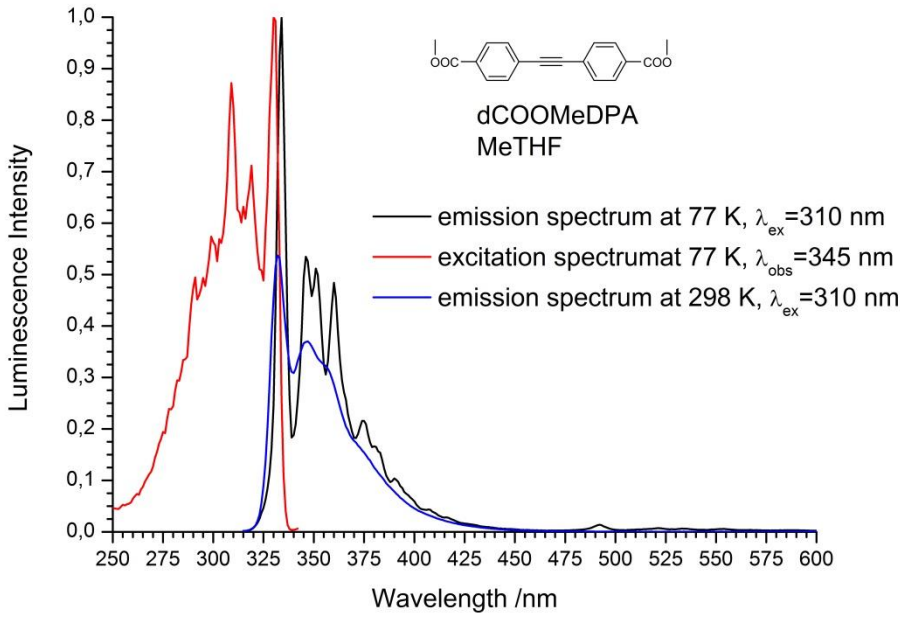


Fig. 20 ESI Luminescence (black line), fluorescence excitation spectrum (red line) measured at 77 K and fluorescence spectrum (blue line) measured at room temperature of dCOOMeDPA in 2-methyltetrahydrofuran.

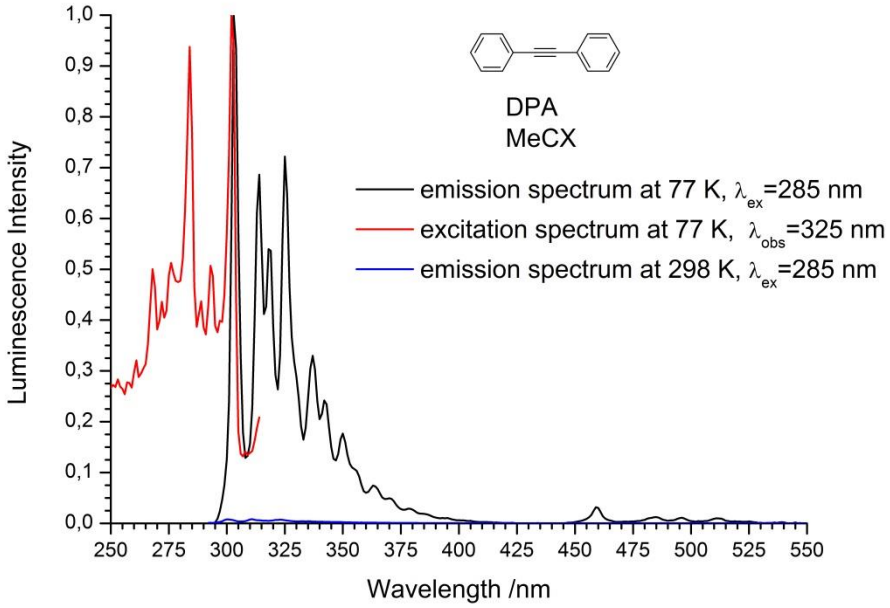


Fig. 21 ESI Luminescence (black line), fluorescence excitation spectrum (red line) measured at 77 K and fluorescence spectrum (blue line) measured at room temperature of DPA in methylcyclohexane.

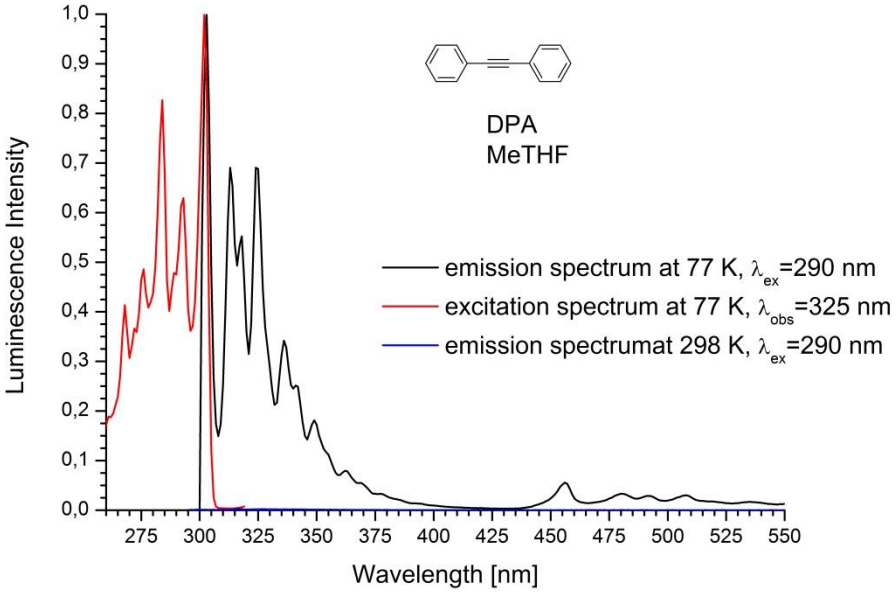


Fig. 22 ESI Luminescence (black line), fluorescence excitation spectrum (red line) measured at 77 K and fluorescence spectrum (blue line) measured at room temperature of DPA in 2-methyltetrahydrofuran.

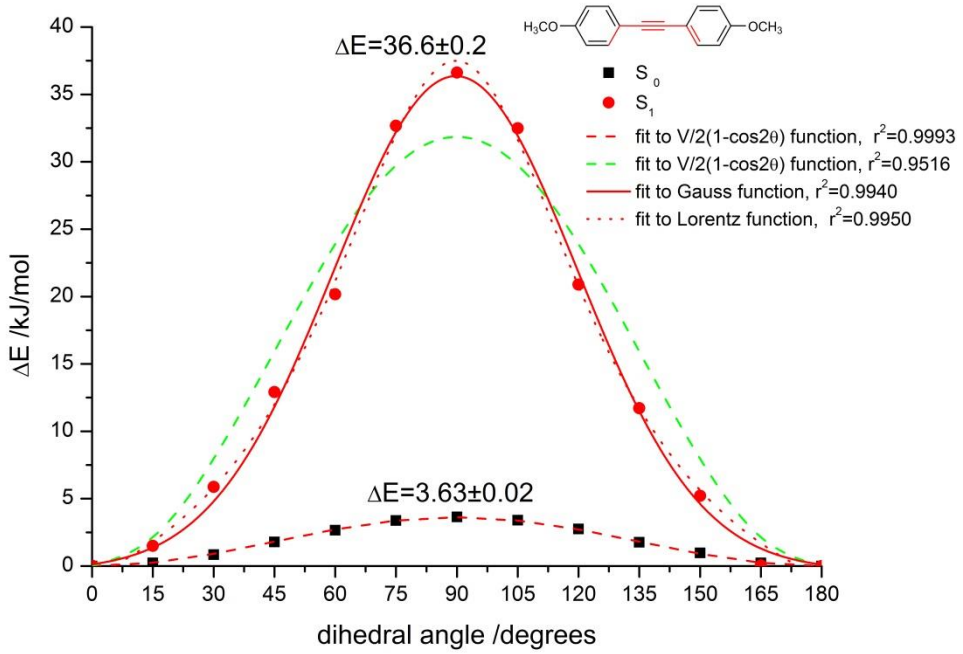


Fig. 23 ESI Potential of rotation energy of C_{Ph}-C≡C bond of dOMeDPA in the ground state (red dashed line) and excited state (red solid line). Dashed lines are the best fit to the equation V/2(1-cos2Θ), whereas the red solid line to the Gauss function and green dotted line to Lorentz function.

Table 6 ESI The energy barrier of rotation of diphenyl acetylene derivatives in the ground and excited state.

derivative	$\Delta E(S_0)$ kJ/mol	ΔE (S_1)kJ/mol
-H	3.8	29.0
-OMe	3.6	36.6
$-N(CH_3)_2$	3.8	34.7
$-COOCH_3$	4.3	36.0
-CN	4.1	35.1
-CHO	4.5	12.7

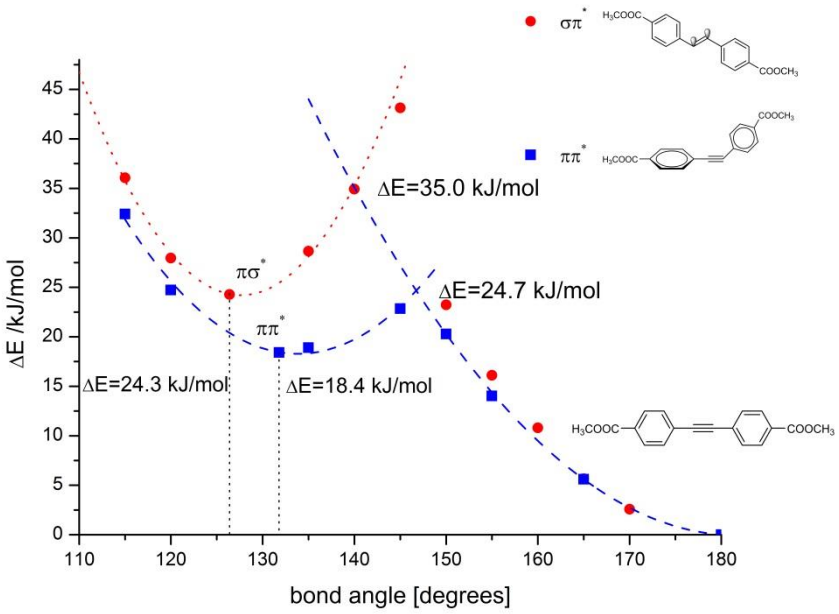


Fig. 24 ESI The energy potential functions of $\pi\pi^*$ (blue squares) and $\sigma\pi^*$ (red dots) states as a C_{Ph}-C≡C bending angle function calculated for dCOOMeDPA. The dashed and dotted line are second order polynomials fitted to the calculated points added for the eyes guide.

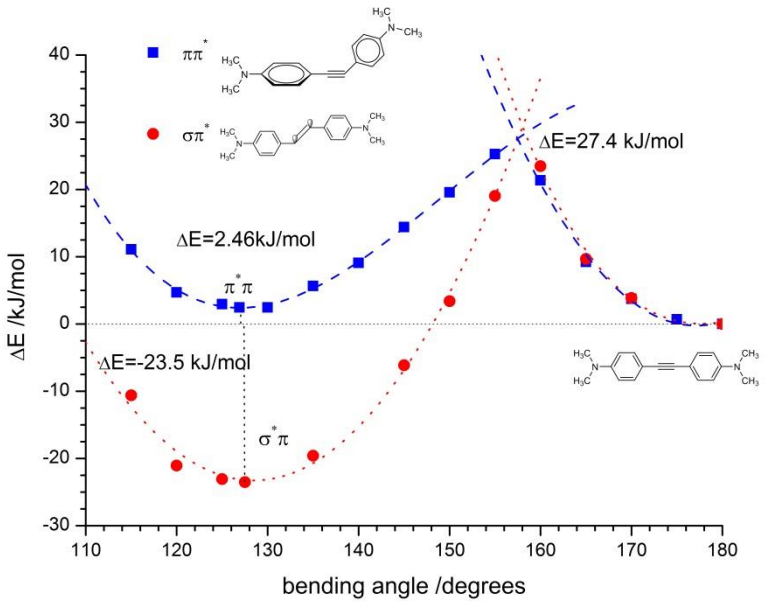


Fig. 25 ESI The energy potential functions of $\pi\pi^*$ (blue squares) and $\sigma\pi^*$ (red dots) states as a C_{Ph}-C≡C bending angle function calculated for dDMADPA. The dashed and dotted line are second order polynomials fitted to the calculated points added for the eyes guide.

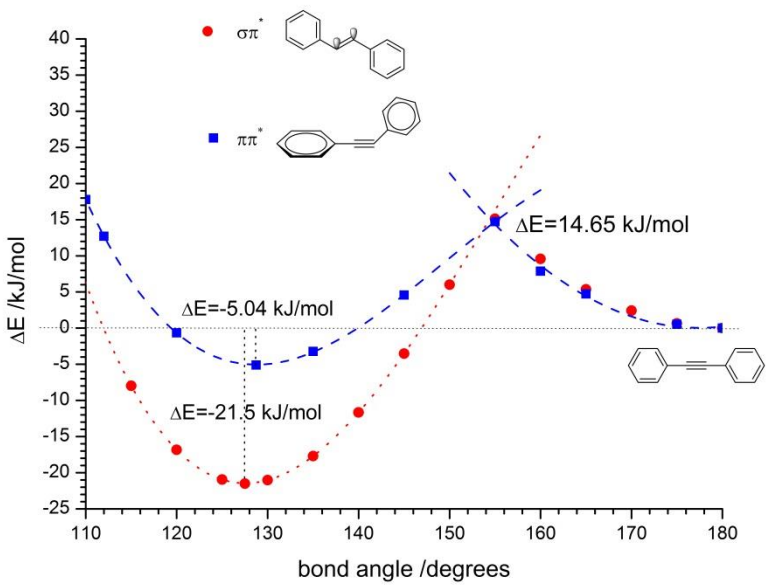


Fig. 26 ESI The energy potential functions of ππ* (blue squares) and σπ* (red dot) states as a C_{Ph}-C≡C bending angle function calculated for DPA. The dashed and dotted line are second order polynomials fitted to the calculated points added for the eyes guide.

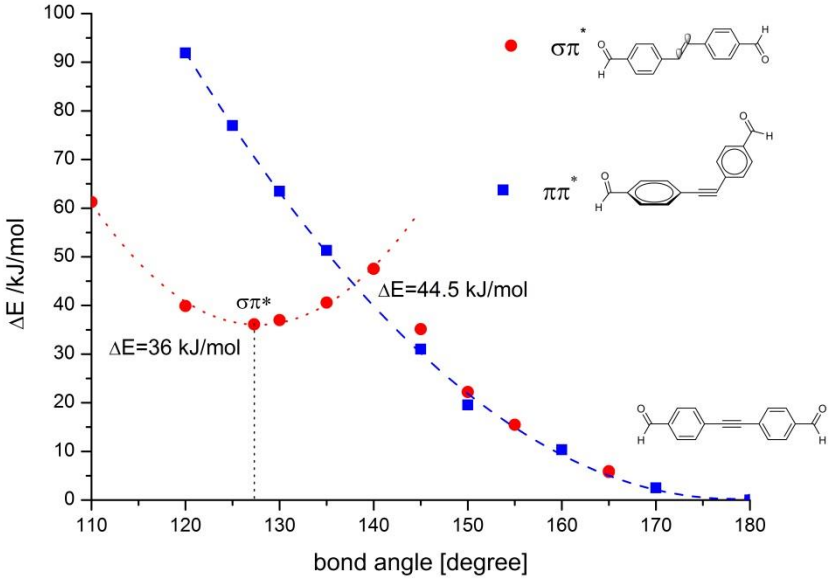


Fig. 27 ESI The energy potential functions of $\pi\pi^*$ (blue square) and $\sigma\pi^*$ (red dot) states as a C_{Ph}-C≡C bending angle function calculated for dCHODPA. The dashed and dotted line are second order polynomials fitted to the calculated points added for the eyes guide.

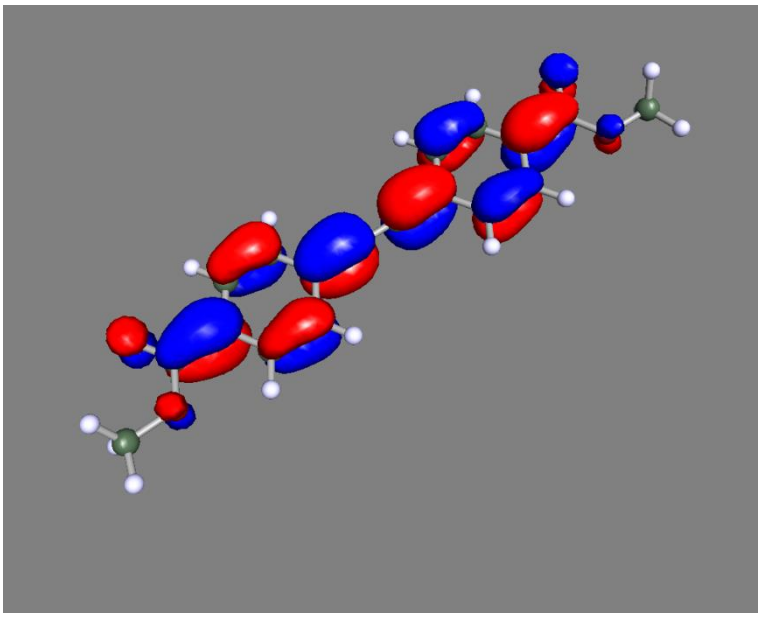


Fig. 28 ESI The frontier orbital of the lowest energy linear structure of dCOOMeDPA in ππ* excited state.

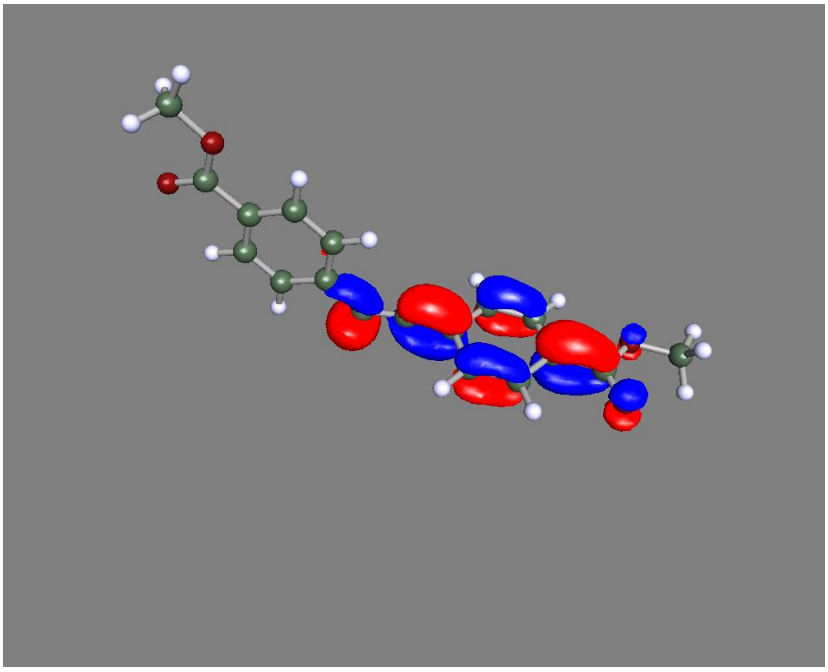


Fig. 29 ESI The frontier orbital of a lowest energy "scorpion like" bent structure of dCOOMeDPA in $\pi\pi^*$ excited state.

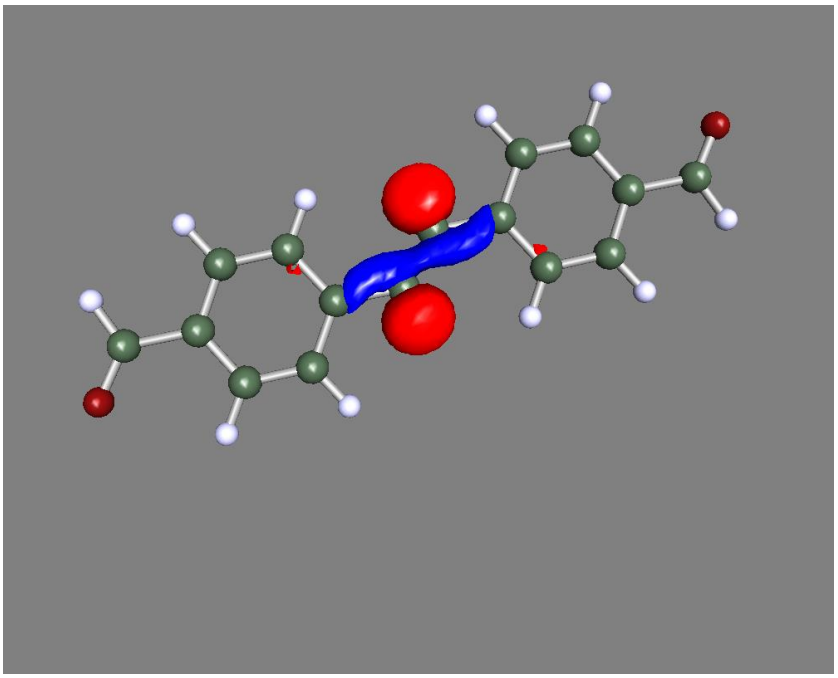


Fig. 30 ESI The frontier orbital of a lowest energy bent structure of dCHODPA in σπ* excited state.

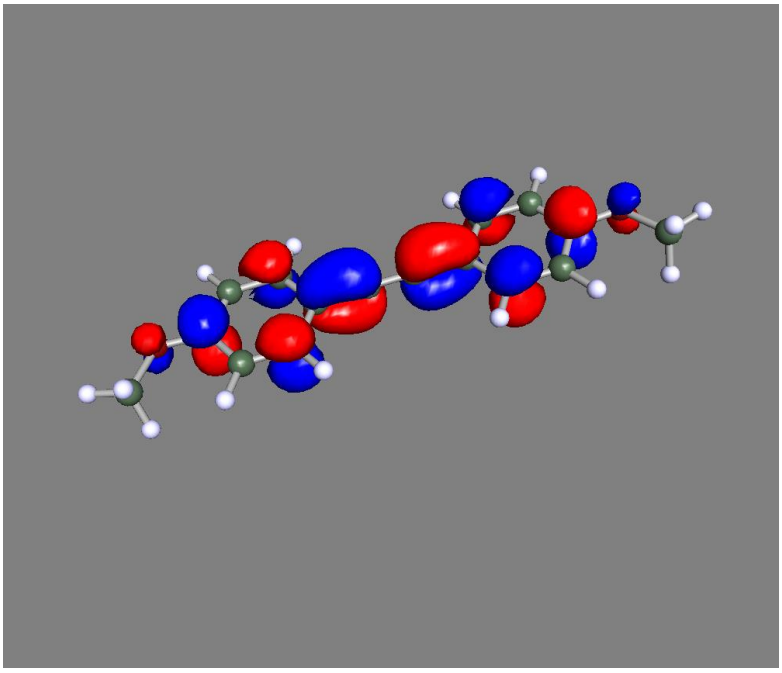


Fig. 31 ESI The frontier orbital of the lowest energy linear structure of dOMeDPA in ππ* excited state.

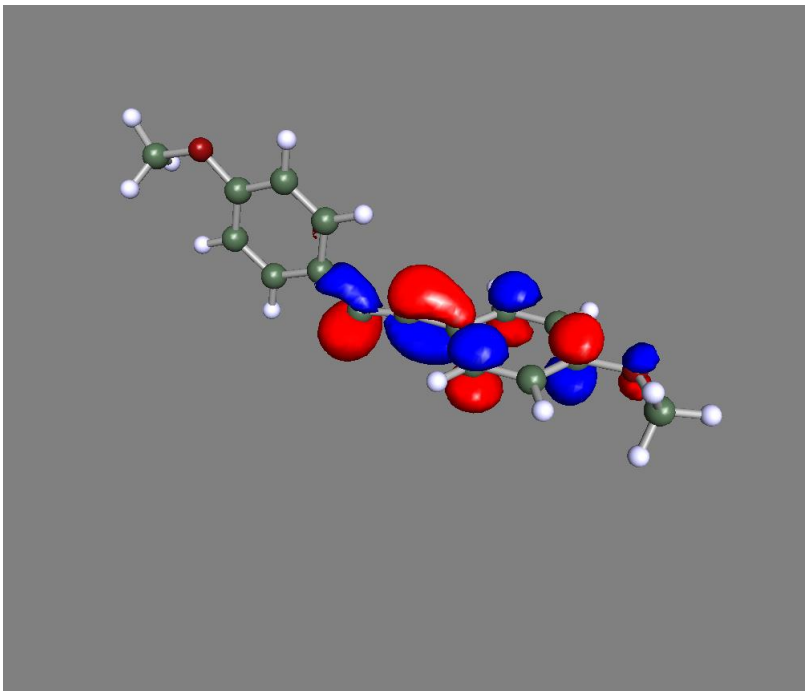


Fig. 32 ESI The frontier orbital of a lowest energy “scorpion like” bent structure of dOMeDPA in ππ* excited state.

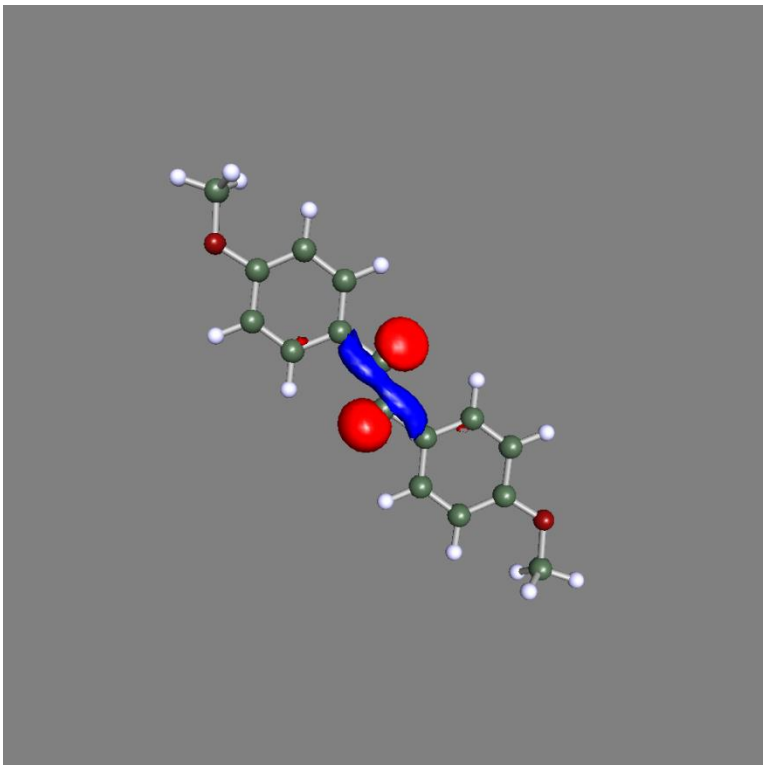


Fig. 33 ESI The frontier orbital of a lowest energy bent structure of dOMeDPA in σπ* excited state.