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Dibenzo[2,3:5,6]pyrrolizino[1,7-*bc*]indolo[1,2,3-*lm*]carbazole: a new electron.

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Supplementary Information.

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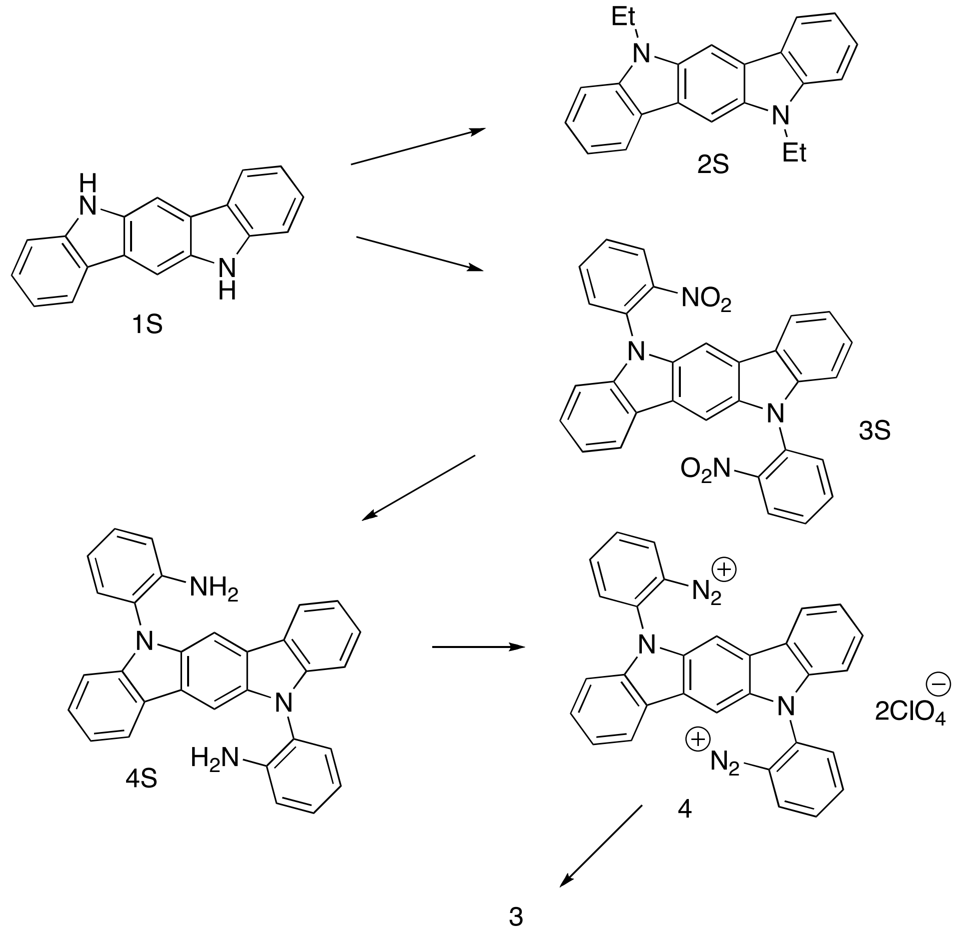
Experimental Part

Route A



5,11-Diethyl-5,11-dihydroindolo[3,2-*b*]carbazole (2S)

5,11-Dihydroindolo[3,2-*b*]carbazole (0.10 g, 0.39 mmol) was dissolved in 50 ml of freshly distilled DMSO under argon. Ethyl bromide (2 ml, 26.82 mmol) and potassium *tert*-butoxide (0.10 g, 0.98 mmol) were added to the mixture, which was stirred for 1.5 h. Another portion of potassium *tert*-butoxide (0.10 g, 0.98 mmol) and ethyl bromide (1.0 ml, 13.41 mmol) were added and the mixture was stirred for additional 1 h. Water (100 ml) was added and the pale brown precipitate was dried to afford 0.11 g of the crude product. The crude product was dissolved in dichloromethane and filtered through silica gel column to afford 0.1 g of pale yellow solid. Crystallization from toluene gave analytically pure sample (0.08 g, 64%) as pale yellow needles, m.p. 277.5 - 278°C.

^{1}H NMR (DMSO-d$_6$) δ, ppm: 1.37 (t, *J* = 7.1 Hz, 6H$_{\text{ethyl}}$), 4.53 (q, *J* = 7.1 Hz, 4H$_{\text{ethyl}}$), 7.18 (t, *J* = 7.7 Hz, 2H$_{2,8}$), 7.45 (t, *J* = 8.1 Hz, 2H$_{3,9}$), 7.56 (d, *J* = 7.7 Hz, 2H$_{4,10}$), 8.26 (d, *J* = 7.6 Hz, 2H$_{1,7}$), 8.33 (s, 2H$_{6,12}$). HRMS Calcd. for $C_{22}H_{20}N_2$: 312.1626; Found: 312.1624. Elemental analysis: calc. (%) for $C_{22}H_{20}N_2$ (312.41) C 84.58, H 6.45, N 8.97; found: C 84.49, H 6.55, N 8.86.

5,11-Bis(2-nitrophenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (3S)

5,11-Dihydroindolo[3,2-*b*]carbazole (1.00 g, 3.91 mmol), anhydrous Na_2CO_3 (3.31 g, 31.2 mmol), Cu (0.1 g, 1.57 mmol) and *o*-iodonitrobenzene (2.14 g, 8.60 mmol) were added to 20 ml of freshly distilled DMSO. The reaction mixture was heated at 130°C for 24 h under argon. After the mixture was cooled down to room temperature, water (200 ml) was added and a pale orange precipitate was filtered and dried. The crude product was dissolved in 1,4-dioxane and filtered. The filtrate was evaporated and the solid residue was washed with acetone to afford 1.41 g (59%) of pale orange powder as a mixture of two atropisomers (A and B). It does not melt up to 300°C.
^1H NMR (DMSO-d_6) δ, ppm, (A): 7.07 (d, *J* = 7.8 Hz, $2H_{4,10}$), 7.24 (t, *J* = 7.3 Hz, $2H_{2,8}$), 7.39 (t, *J* = 7.3 Hz, $2H_{3,9}$), 7.92 (t, *J* = 7.8 Hz, $2H_{phenyl,}$), 7.97 (s, $2H_{6,12}$), 8.02 (d, *J* = 7.8 Hz, $2H_{phenyl}$), 8.08 (t, *J* = 7.8 Hz, $2H_{phenyl}$), 8.26 (d, *J* = 7.3 Hz, $2H_{1,7}$), 8.36 (d, *J* = 8.3 Hz, $2H_{phenyl}$); (B): 7.06 (d, *J* = 8.3 Hz, $2H_{4,10}$), 7.24 (t, *J* = 7.3 Hz, $2H_{2,8}$), 7.39 (t, *J* = 7.3 Hz, $2H_{3,9}$), 7.92 (t, *J* = 7.8 Hz, $2H_{phenyl,}$), 7.95 (d, *J* = 8.3 Hz, $2H_{phenyl}$), 7.99 (s, $2H_{6,12}$), 8.10 (t, *J* = 7.3 Hz, $2H_{phenyl}$), 8.27 (d, *J* = 7.8 Hz, $2H_{1,7}$), 8.38 (d, *J* = 8.3 Hz, $2H_{phenyl}$). HRMS Calcd. for $C_{30}H_{18}N_4O_4$: 498.1328, Found: 498.1330. Elemental analysis: calc. (%) for $C_{30}H_{18}N_4O_4$ (498,49) C 72.28, H 3.64, N 11.24; found: C 72.18, H 3.69, N 11.11.

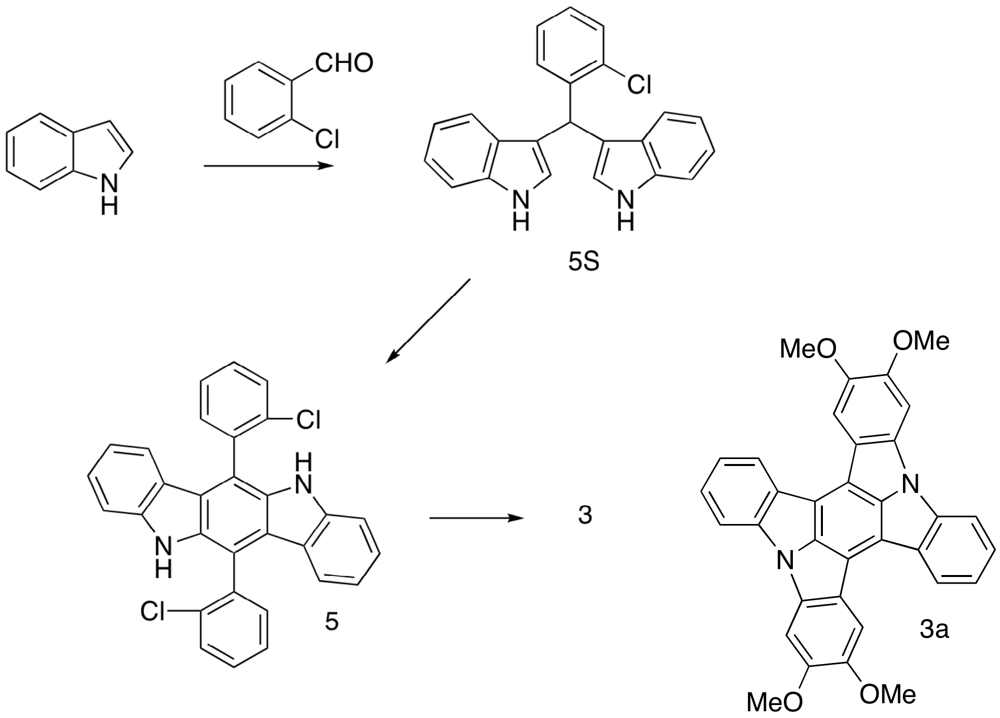
2-[11-(2-Aminophenyl)indolo[3,2-*b*]carbazol-5(11*H*)-yl]aniline (4S)

Derivative **3S** (0.50 g, 1.14 mmol) and $SnCl_2{*}2H_2O$ (2.26 g, 10.0 mmol) were dissolved in 20 mL of ethyl acetate under argon. The reaction mixture was heated at 70°C for 6 h with constant stirring. After cooling down to room temperature, the reaction mixture was poured into 100 mL of ice water and a saturated solution of sodium hydroxide was added until pH = 13. The heavy yellowish precipitate was extracted with 4x40 mL portions of ethyl acetate. The combined extracts were washed with brine, treated with charcoal and filtered. Evaporation of the filtrate afforded 0.26 g (61%) of yellowish micro crystals, as a mixture of atropisomers. It does not melt up to 300°C.
^1H NMR (DMSO-d6) δ, ppm (A): 4.81 (s, $4H_{NH2}$), 6.81 (t, *J* = 7.5 Hz, $2H_{phenyl}$), 7.02 (d, *J* = 8.1 Hz, $2H_{phenyl}$), 7.05 (d, *J* = 8.1 Hz, $2H_{phenyl}$), 7.17 (t, *J* = 7.2 Hz, $2H_{2,8}$), 7.19 (d, *J* = 7.8 Hz, $2H_{4,10}$), δ 7.31 (t, *J*= 7.8 Hz, $2H_{phenyl}$), δ 7.37 (t, *J* = 8.1 Hz, $2H_{3,9}$), 7.78 (s, $2H_{6,12}$), 8.22 (d, *J* = 7.8 Hz, $2H_{1,7}$); (B): 4.76 (s, $4H_{NH2}$), 6.81 (t, *J* = 7.5 Hz, $2H_{phenyl}$), 7.02 (d, *J* = 8.1 Hz, $2H_{phenyl}$), 7.05 (d, *J* = 8.1 Hz, $2H_{phenyl}$), 7.17 (t, *J* = 7.2 Hz, $2H_{2,8}$), 7.21 (d, *J* = 7.8 Hz, $2H_{4,10}$), 7.31 (t, *J* = 7.8, $2H_{phenyl}$), 7.37 (t, *J* = 7.8 Hz, $2H_{3,9}$), 7.79 (s, $2H_{6,12}$), 8.22 (d, *J* = 7.8 Hz, $2H_{1,7}$). HRMS Calcd. for $C_{30}H_{22}N_4$: 438.1844, Found: 438.1832. Elemental analysis: calc. (%) for $C_{30}H_{22}N_4$ (438,52) C 82.17, H 5.06, N 12.78; found: C 82.28, H 5.11, N 12.66.

1,2-[11-(2-Diazyn-1-iumylphenyl)indolo[3,2-*b*]carbazol-5(11*H*)-yl]phenyldiazonium perchlorate (4)

Derivative **4S** (0.10 g, 0.23 mmol) was suspended in 7 ml of acetic acid. A solution of 3 mL of concentrated sulfuric acid in 2 ml of water was added dropwise to the mixture. The resulting yellow solution was cooled to 5°C in an ice bath, and a solution of sodium nitrite (0.05 g, 0.72 mmol) in 2 ml of water was added in one portion. The resulting purple solution was diluted with 10 ml of water and 7 ml of 60% perchloric acid was added in one portion. The fine purple precipitate was filtered in the dark, washed with water and dried to afford 0.15 g (98%) of purple solid as a mixture of two atropisomers ^{1}H NMR (DMSO-d_6) δ, ppm (A and B): 7.49 (t, *J* = 7.7 Hz, 2H$_{2,8}$), 7.60 (t, *J* = 8.4 Hz, 2H$_{3,9}$), 7.68 (d, *J* = 8.0 Hz, 2H$_{4,10}$), 8.18 (t, *J* = 8.4 Hz, 2H$_{\text{phenyl}}$), 8.40 (d, *J* = 8.4 Hz, 2H$_{1,7}$), 8.44 (d, *J* = 8.4Hz, 2H$_{\text{phenyl}}$), 8.58 (s, 2H$_{6,12}$), 8.58 (t, *J* = 8.4 Hz, 2H$_{\text{phenyl}}$), 9.07 (d, *J* = 8.4 Hz, 2H$_{\text{phenyl}}$).

Route B



3-[(2-chlorophenyl)(1*H*-indol-3-yl)methyl]-1*H*-indole 5S:

A solution of indole (4.99 g, 42.65 mmol) and 2-chlorobenzaldehyde (3.00 g, 21.34 mmol) in methanol (60 ml) was refluxed for 24 h. The reaction mixture was then cooled down at room temperature and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel using cyclohehexane-dichoromethane (2:1) as eluent. Pure **5S** (3.83 g, 50%) was obtained as a white powder.

m.p : 69-70°C (lit.[1] 70-71°C). ^{1}H NMR (CDCl$_3$): δ = 7.65 (br s, 2H), 6.80-7.30 (m, 12H), 6.42 (s, 2H), 6.17 (s, 1H).

3-[(2-bromo-4,5-dimethoxyphenyl)(1*H*-indol-3-yl)methyl]-1*H*-indole was prepared analogously from indole and 2-bromo-4,5-dimethoxybenzaldehyde in 80% yield and was used on the next step without further purification.

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[1] Ji, S.-J.; Wang, S.-Y.; Zhang, Y.; Loh, T.-P. *Tetrahedron* **2004**, *60*, 2051.

6,12-bis(2-chlorophenyl)-5,11-dihydroindolo[3,2-*b*]carbazole 5:

Iodine (0.03 g, 0.12 mmol) was added to a solution of **5S** (2.20 g, 6.16 mmol) in 10 ml of acetonitrile. The reaction mixture was refluxed for 2h. The precipitated product was filtered, washed with acetonitrile and dried to afford pure **5** (0.18 g) as a colorless powder in 12% yield. Iodine (0.03 g, 0.12 mmol) was added to the filtrate and the mixture was refluxed for another 3h. Additional amount of **5** (0.19 g) precipitated from the reaction mixture. The overall yield was 25%. It was used on the next step without further purification.

m.p. : > 300°C. ^{1}H NMR (DMSO-d$_6$): δ = 10.81 (br. s, 2H), 6.77-7.28 (m, 16H).

6,12-bis(2-bromo-4,5-dimethoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole was obtained analogously in 48% yield and was used on the next step without further purification.

Dibenzo[2,3:5,6]pyrrolizino[1,7-*bc*]indolo[1,2,3-*lm*]carbazole (3)

^{1}H NMR (in CS$_2$, referenced to acetone d-6) δ, ppm: 6.78 (t, J = 7.4 Hz, 4H$_{2,8,11,17}$), 6.93 (t, 7.4 Hz, 4H$_{3,7,12,16}$), 7.33 (d, J = 8.1 Hz, 4H$_{4,6,13,15}$), 7.80 J = 8.1 Hz, 4H$_{1,9,10,18}$)

2,3,11,12-tetramethoxydibenzo[2,3:5,6]pyrrolizino[1,7-*bc*]indolo[1,2,3-*lm*]carbazole 3a was prepared by the same procedure as a yellow powder in 75% yield.

It does not melt up to 350°C and sublimes at higher temperature. HRMS Calcd. for $C_{34}H_{24}N_2O_4$: 524.1736; Found: 524.1766. Elemental analysis: calc. (%) for $C_{34}H_{24}N_2O_4$ (524.57) C 77.85, H 4.61, N 5.34; found: C 77.97, H 4.55, N 5.26

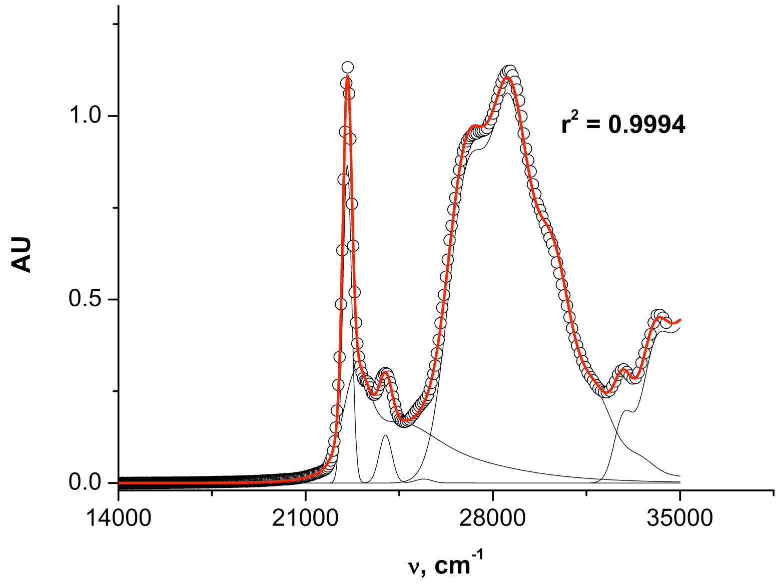

Figure 1S. Fitting the OPA spectrum of **3** in toluene with four Pekarian functions. Circles: the experimental spectrum; red curve: the sum of the Pekarians (black curves).

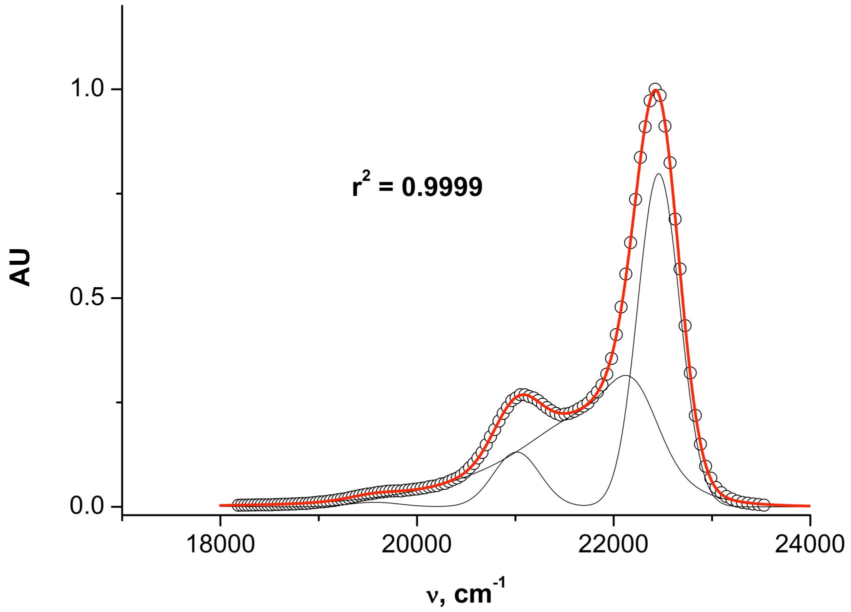

Figure 2S. Fitting the fluorescence spectrum of **3** in toluene with two Pekarian functions. Circles: the experimental spectrum; red curve: the sum of the Pekarians (black curves).

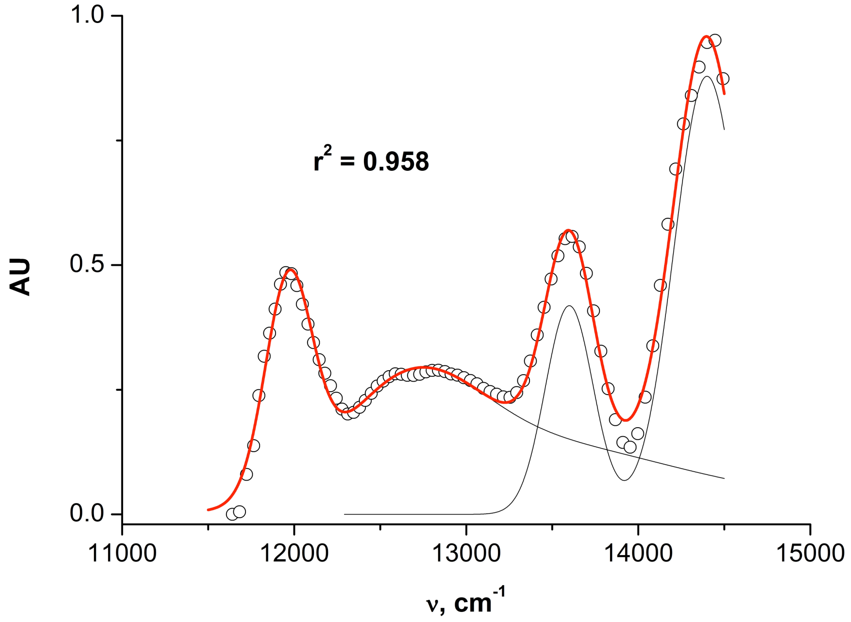

Figure 3S. Fitting the TPA absorption of **3** in toluene with two Pekarian functions. Circles: the experimental spectrum; red curve: the sum of the Pekarians (black curves).

Table 1S. Electronic transitions of **3** derived from deconvolution of the experimental spectra and calculated by the TD B3LYP method.

Experimental (from fitting)		Calculated TD B3LYP/6-31G(d,p)				
λ_{max} (nm)	Area (a.u.)	λ_{max} (nm)[b]	Oscillator strength	λ_{max} (nm)[c]	Oscillator strength	Orbitals involved
438	0.4	416	0.14	421	0.22	105-106
405	1.1	363	0.11	365	0.16	102-106
385[a]	0.56	376	0	378	0	103-106
348	4.57	352	0.70	362	0.95	104-106
292[a]	0.47	291	0	292	0	101-106
279	0.55	284	0.05	284	0.07	105-108

[a] From the TPE spectrum $\lambda_{max}/2$. [b] Calculated in vac. [c] Calculated in toluene.

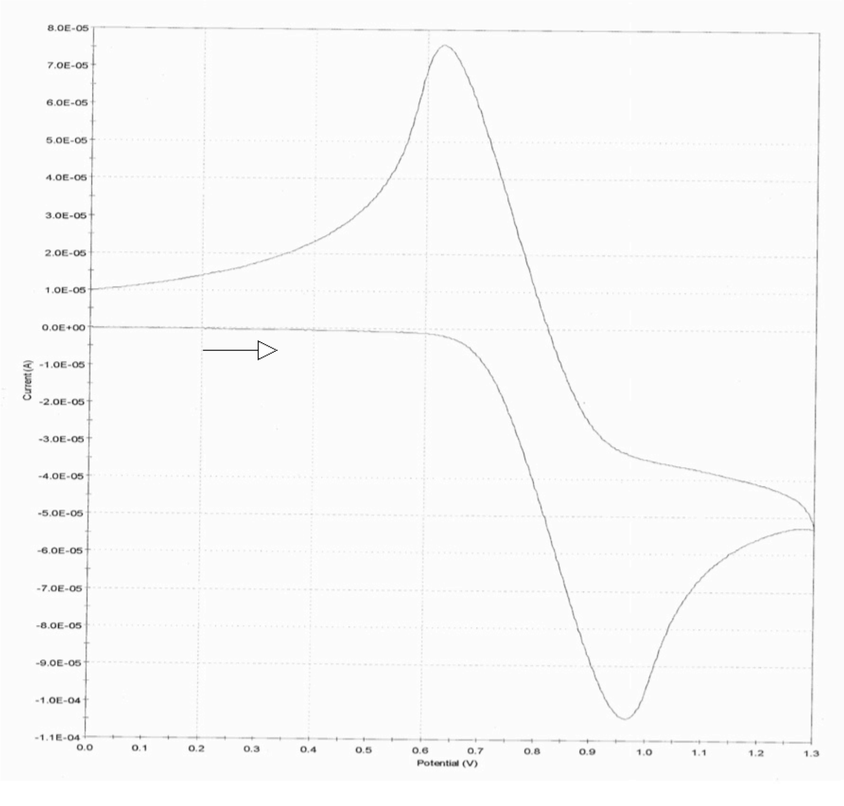

Figure 4S. A CV of **2S** in DMSO/tetrabutylammonium perchlorate (0.1 mol/L), Ag/AgCl reference electrode, glassy carbon working electrode, sweep rate 100 mV/s.

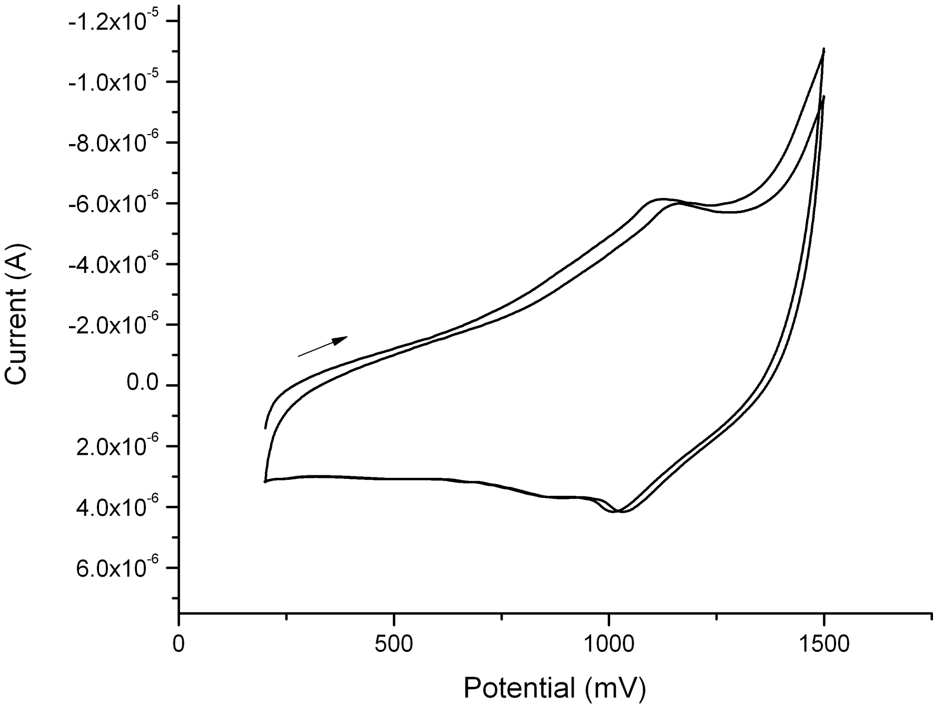

Figure 5S. A CV of **3** in DMSO/tetrabutylammonium perchlorate (0.1 mol/L), Ag/AgCl reference electrode, glassy carbon working electrode, sweep rate 100 mV/s

Cyclic voltammetry measurements were performed using the classical three-electrode cell under nitrogen on Princeton Applied Research (PAR) Potentiostate/Galvanostate Model 173 and PAR Universal Programmer Model 175.

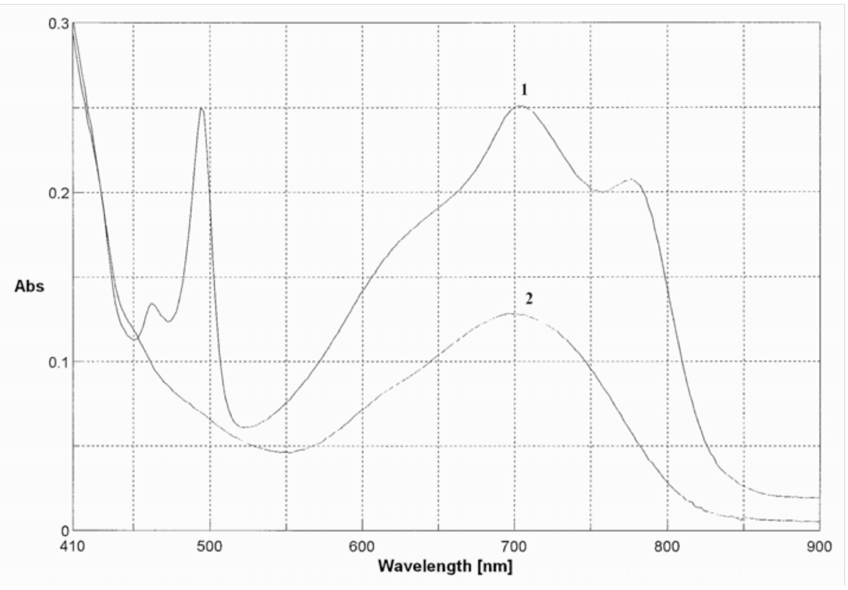

Figure 6S. Absorption spectra of **3** radical cation perchlorate in PhCN. 1: freshly prepared salt solution; 2. After 24 h.

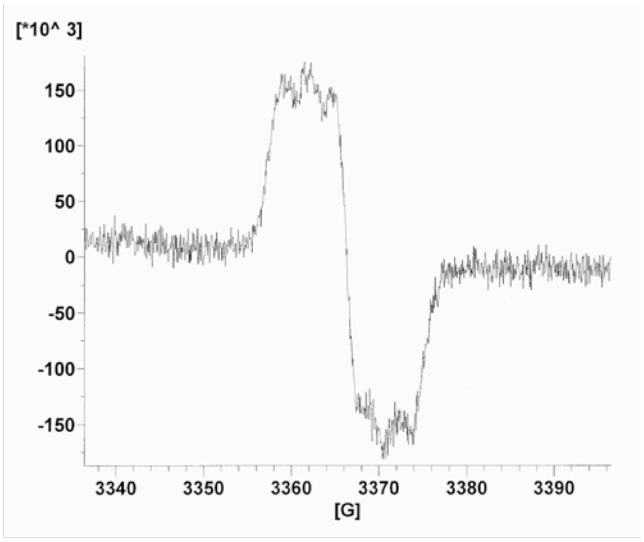

Figure 7S. EPR spectrum of **3** cation radical perchlorate in PhCN.