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Supporting Information

One-Electron Reduced and Oxidized Stages of Donor-substituted 1,1,4,4-Tetracyanobuta-1,3-dienes of Different Molecular Architectures

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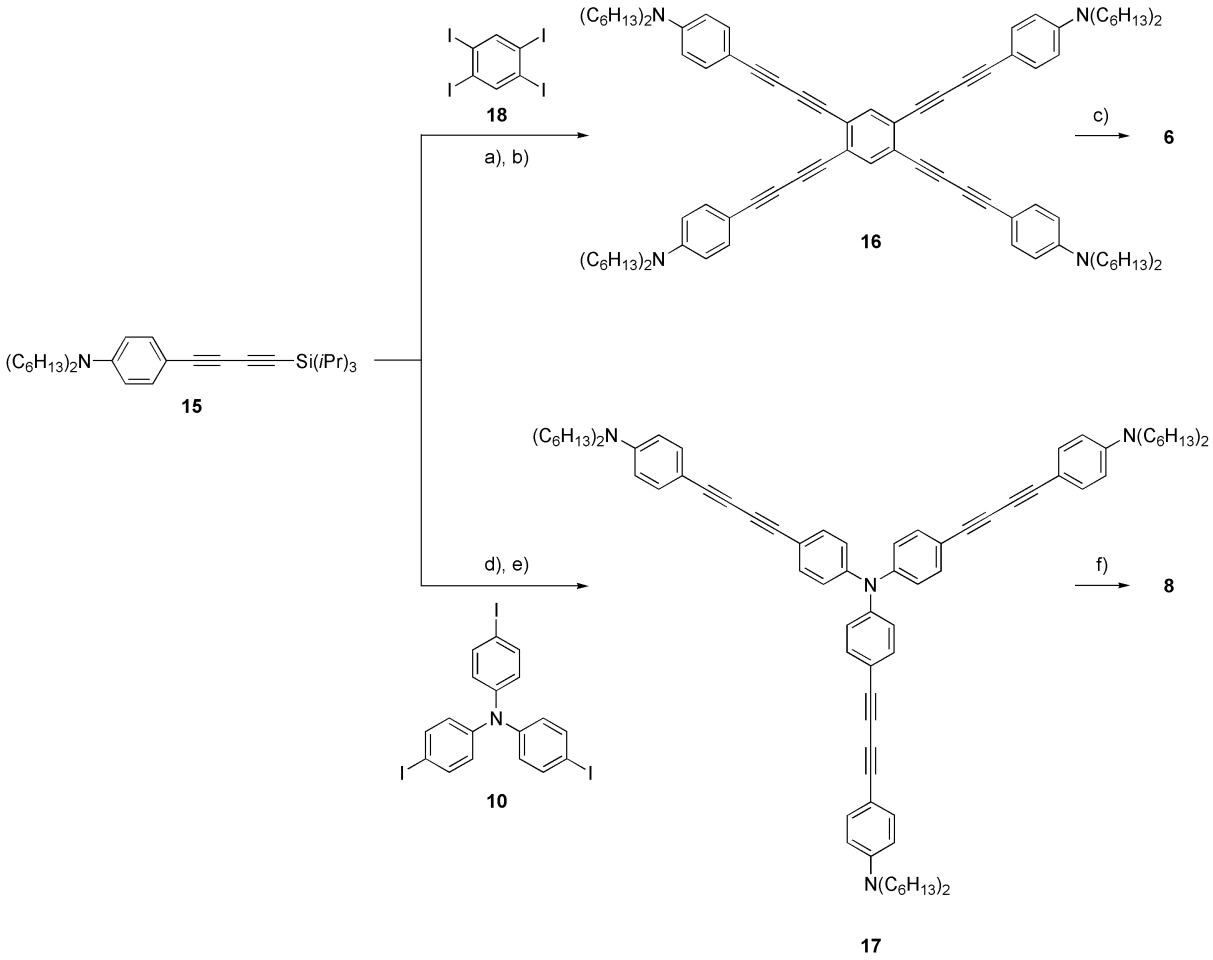
Experimental Section

Materials and general methods: For most information, see the Experimental Section in the main manuscript. Additional details: 1,2,4,5-Tetraiodobenzene (**18**) was prepared according to literature procedure.[1]

Electrochemistry: The electrochemical measurements were carried out at 20 °C in CH_2Cl_2, containing 0.1 M nBu$_4$NPF$_6$ in a classical three-electrode cell. CH_2Cl_2 was purchased in spectroscopic grade from Merck, dried over molecular sieves (4 Å) and stored under Ar prior to use. nBu$_4$NPF$_6$ was purchased in electrochemical grade from Fluka and used as received. The working electrode was a glassy carbon disk electrode (3 mm in diameter) used either motionless for cyclic voltammetry (0.1 to 10 V s^{-1}) or as rotating-disk electrode for rotating disk voltammetry (RDV). The auxiliary electrode was a Pt wire, and the reference electrode was either an aqueous Ag/AgCl electrode or a platinum wire used as a pseudo reference

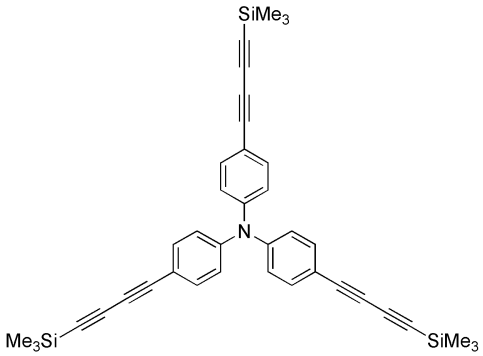
electrode. All potentials are referenced to the ferricinium/ferrocene (Fc^+/Fc) couple, used as an internal standard, and are uncorrected from ohmic drop. The cell was connected to Autolab PGSTAT20 potentiostat (Eco Chemie BV, Utrecht, The Netherlands) controlled by the GPSE software running on a personal computer.



Scheme 1SI: Synthesis of dendritic charge-transfer chromophores **6** and **8**. a) nBu$_4$NF, THF, 20 min, 0 °C. b) 1,2,4,5-tetraiodobenzene (**18**), [$PdCl_2(PPh_3)_2$], CuI, (iPr)$_2$NH, 24 h, 60 °C, 24% (**16**) (yield over two steps). c) TCNE, CH_2Cl_2, 18 h, 20 °C, 98% (**6**). d) nBu$_4$NF, THF, 20 min, 0 °C. e) tris(4-iodophenyl)amine (**10**), [$PdCl_2(PPh_3)_2$], CuI, (iPr)$_2$NH, 16 h, 20 °C, 100% (**17**) (yield over two steps). f) TCNE, CH_2Cl_2, 16 h, 20 °C, 100% (**8**).

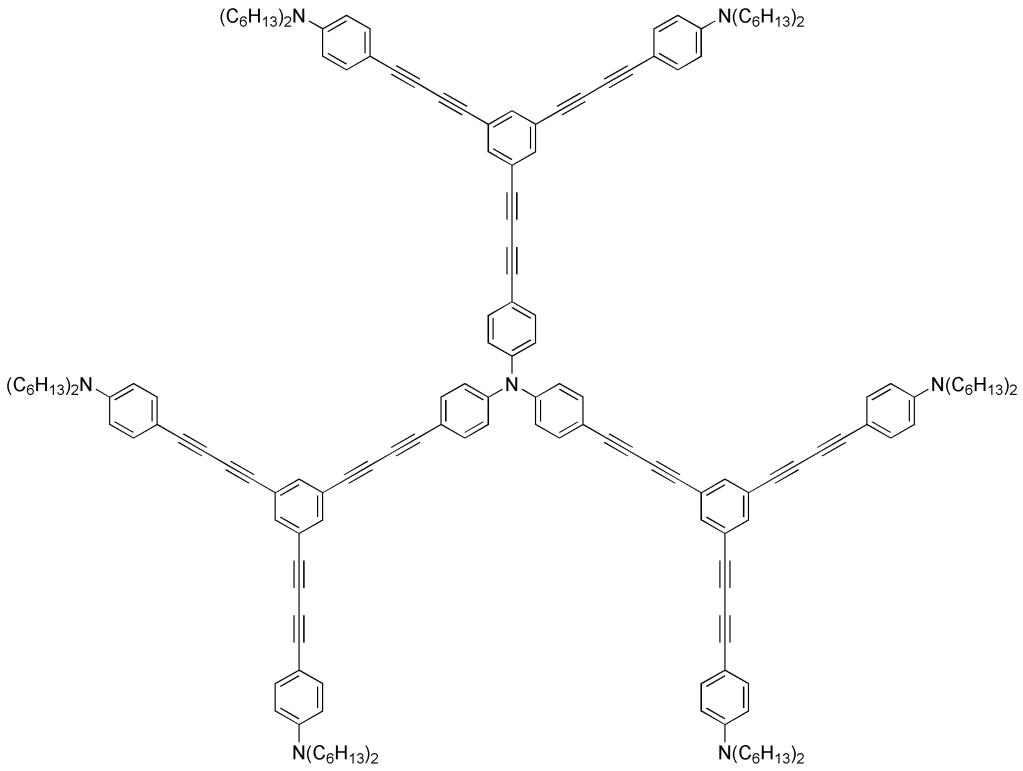
Synthetic Protocols:

4-[4-(Trimethylsilyl)buta-1,3-diyn-1-yl]-*N*,*N*-bis{4-[4-(trimethylsilyl)buta-1,3-diyn-1-yl]phenyl}aniline (11)



To a solution of 1,4-bis(trimethylsilyl)buta-1,3-diyne (468 mg, 2.40 mmol) in THF (25 mL), MeLi·LiBr (2.2 M in Et_2O, 1.10 mL, 2.40 mmol) was added and the mixture stirred for 3 h at 20 °C. Saturated aq. NH_4Cl solution (10 mL) was added and the mixture extracted with *n*-pentane (3 × 20 mL). The combined organic layers were washed with saturated aq. NaCl solution (2 × 20 mL), dried ($MgSO_4$), and concentrated *in vacuo* without heating to *ca.* 10% of the original volume. The residue was dissolved in diisopropylamine (30 mL), tris(4-iodophenyl)amine (**10**) (100 mg, 0.16 mmol) and the mixture deoxygenated thoroughly by bubbling Ar through for 30 min. CuI (9 mg, 0.048 mmol) and [$PdCl_2(PPh_3)_2$] (22 mg, 0.032 mmol) were added, and the mixture was stirred under Ar for 13 h at 20 °C. The mixture was concentrated *in vacuo* and the residue subjected to CC (SiO_2, hexanes/CH_2Cl_2 5:1) to give **11** (98 mg, 100%). Brown solid. m.p. 100–105 °C (decomp.); R_f = 0.54 (SiO_2, hexanes/CH_2Cl_2 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): d = 0.23 (*s*, 27 H), 6.98 (*d*, J = 8.7, 6 H), 7.37 ppm (*d*, J = 8.7, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): d = –0.18, 74.46, 76.72, 88.12, 90.99, 116.45, 124.23, 134.21, 147.25 ppm; IR (neat): $\tilde{n}$ = 2958*w*, 2197*m*, 2101*m*, 1591*s*, 1499*s*, 1409*w*, 1317*s*, 1288*s*, 1268*m*, 1246*s*, 1177*m*, 1105*w*, 1027*m*, 1009*m*, 826*s* cm^{-1}; UV/Vis (CH_2Cl_2): l_{max} (e) = 264 (22800), 279 (28800), 297 (25600), 381 nm (100700); HR-MALDI-MS (DCTB): *m*/*z*: 605.2376 ([M]$^+$, $C_{39}H_{39}NSi_3^+$, calc. 605.2385); Anal. calc. for $C_{39}H_{39}NSi_3$ (606.00): C 77.30, H 6.49, N 2.31; found: C 77.46, H 6.75, N 2.20.

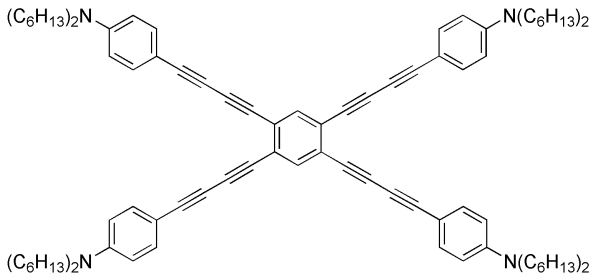
4,4',4'',4''',4'''',4''''' '-[Nitrilotris(4,1-phenylenebuta-1,3-diyne-4,1-diylbenzene-5,1,3-triyldibuta-1,3-diyne-4,1-diyl)]hexakis(*N*,*N*-dihexylaniline) (13)



To a solution of **11** (30 mg, 0.049 mmol) in THF (10 mL), *n*Bu$_4$NF (1.0 M in THF, 0.30 mL) was added. The mixture was stirred for 20 min at 0 °C, diluted with CH_2Cl_2, filtered through a plug (SiO_2, CH_2Cl_2), and the solution was concentrated *in vacuo* to *ca.* 10% of the original volume. The residue was dissolved in diisopropylamine (15 mL), iododerivative **12** (162 mg, 0.198 mmol) was added, and the mixture deoxygenated thoroughly by bubbling N_2 through for 30 min. CuI (3.0 mg, 0.015 mmol) and [$PdCl_2(PPh_3)_2$] (7.0 mg, 0.010 mmol) were added, and the mixture was stirred under N_2 for 15 h at 20 °C. The mixture was concentrated *in vacuo* and the residue subjected to CC (SiO_2, hexanes/CH_2Cl_2 5:1 → 2:1) to give **13** (56 mg, 46%). Yellow greasy solid. R_f = 0.50 (SiO_2, hexanes/CH_2Cl_2 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): *d* = 0.92 (*t*, *J* = 6.5, 36 H), 1.31 (*s*, 72 H), 1.55 (*m*, 24 H), 3.27 (*t*, *J* = 7.6, 24 H), 6.53 (*d*, *J* = 8.7, 12 H), 7.05 (*d*, *J* = 8.4, 6 H), 7.37 (*d*, *J* = 8.7, 12 H), 7.45 (*d*, *J* = 8.4, 6 H), 7.55 ppm (*s*, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): *d* = 14.25, 22.88, 26.98, 27.34, 31.89, 51.15, 71.90, 74.01, 75.67, 78.73, 79.85, 82.49, 85.22, 106.24, 111.29, 116.59, 123.08, 123.86, 124.30, 134.20, 134.36, 135.65, 147.35, 148.89 ppm (24 out of 26 signals expected); IR (neat): $\tilde{n}$ = 2924*m*, 2854*m*, 2202*s*, 2137*w*, 1598*s*, 1575*s*, 1517*s*, 1505*s*, 1463*m*, 1402*m*,

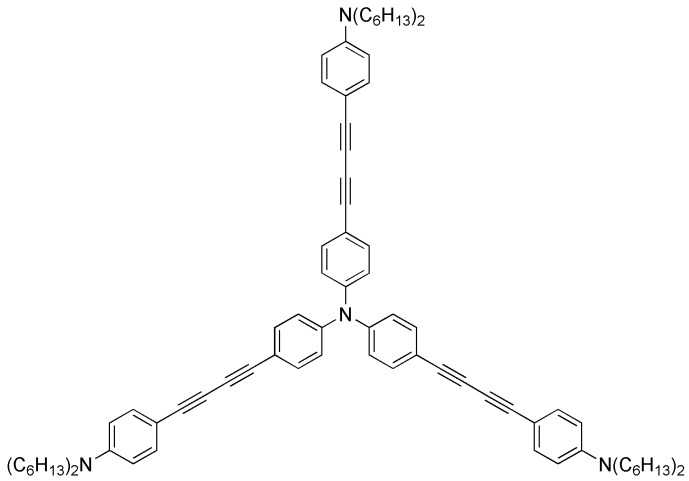
1362*s*, 1317*m*, 1288*m*, 1254*m*, 1191*s*, 1163*s*, 1105*m*, 1057*w*, 979*w*, 873*m*, 830*m*, 809*s* cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (*e*) = 273 (146700), 289 (151100), 307 (152800), 322 (sh, 160000), 344 (208600), 401 nm (346000); HR-MALDI-MS (DCTB): *m*/*z*: 2461.5896 ([*M*H]$^+$, $C_{180}H_{202}N_7^+$, calc. 2461.6022).

4,4',4'',4'''-(Benzene-1,2,4,5-tetrayltetrabuta-1,3-diyne-4,1-diyl)tetrakis(*N*,*N*-dihexylaniline) (16)



To a solution of **15** (720 mg, 1.55 mmol) in THF (20 mL), *n*Bu_4NF (1.0 M in THF, 4.6 mL) was added. The mixture was stirred for 30 min at 0 °C, diluted with CH_2Cl_2, filtered through a plug (SiO_2, CH_2Cl_2), and the solvents were removed *in vacuo*. The residue was dissolved in diisopropylamine (50 mL), 1,2,4,5-tetraiodobenzene (**18**) (150 mg, 0.26 mmol) was added and the mixture deoxygenated thoroughly by bubbling N_2 through for 30 min. CuI (15 mg, 0.077 mmol) and [$PdCl_2(PPh_3)_2$] (36 mg, 0.051 mmol) were added, and the mixture was stirred under N_2 for 24 h at 60 °C. The mixture was diluted with CH_2Cl_2 and passed through a plug (SiO_2, CH_2Cl_2), and the solvents were removed *in vacuo*. The residue was subjected to CC (SiO_2, hexanes/CH_2Cl_2 5:1 → 2:1) to give **16** (82 mg, 24%). Orange greasy solid. R_f = 0.50 (SiO_2, hexanes/CH_2Cl_2 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): *d* = 0.92 (*t*, *J* = 6.4, 24 H), 1.33 (*s*, 48 H), 1.59 (*m*, 16 H), 3.28 (*t*, *J* = 7.6, 16 H), 6.54 (*d*, *J* = 9.0, 8 H), 7.40 (*d*, *J* = 9.0, 8 H), 7.58 ppm (*s*, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): *d* = 14.25, 22.89, 26.98, 27.36, 31.89, 51.16, 72.59, 78.31, 81.66, 87.12, 106.50, 111.28, 125.40, 134.41, 137.23, 148.88 ppm; IR (neat): $\tilde{\nu}$ = 2924*m*, 2854*m*, 2192*s*, 2138*w*, 1596*s*, 1519*s*, 1483*s*, 1465*m*, 1402*m*, 1363*s*, 1293*m*, 1254*m*, 1227*w*, 1199*m*, 1174*s*, 1107*w*, 1020*w*, 994*w*, 896*w*, 810*s* cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (*e*) = 295 (sh, 62000), 333 (sh, 134800), 350 (161400), 397 (94000), 464 nm (114300); HR-MALDI-MS (3-HPA): *m*/*z*: 1307.9766 ([*M*H]$^+$, $C_{94}H_{123}N_4^+$, calc. 1307.9748).

4,4',4''-[Nitrilotris(4,1-phenylenebuta-1,3-diyne-4,1-diyl)]tris(*N*,*N*-dihexylaniline) (17)



To a solution of **15** (336 mg, 0.72 mmol) in THF (15 mL), *n*Bu_4NF (1.0 M in THF, 1.6 mL) was added. The mixture was stirred for 20 min at 0 °C, diluted with CH_2Cl_2, and filtered through a plug (SiO_2, CH_2Cl_2), and the solvents were removed *in vacuo*. The residue was dissolved in diisopropylamine (25 mL), tris(4-iodophenyl)amine (**10**) (100 mg, 0.16 mmol) was added, and the mixture deoxygenated thoroughly by bubbling N_2 through for 30 min. CuI (9.0 mg, 0.048 mmol), and $[PdCl_2(PPh_3)_2]$ (22 mg, 0.032 mmol) were added, and the mixture was stirred under N_2 for 16 h at 20 °C. The mixture was diluted with CH_2Cl_2 and passed through a plug (SiO_2, CH_2Cl_2), and the solvents were removed *in vacuo*. The residue was subjected to CC (SiO_2, hexanes/CH_2Cl_2 4:1) to give **17** (194 mg, 100%). Orange greasy solid. R_f = 0.33 (SiO_2, hexanes/CH_2Cl_2 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 0.89 (*t*, *J* = 6.8, 18 H), 1.30 (*s*, 36 H), 1.55 (*m*, 12 H), 3.25 (*t*, *J* = 7.7, 12 H), 6.50 (*d*, *J* = 9.1, 6 H), 6.99 (*d*, *J* = 8.8, 6 H), 7.33 (*d*, *J* = 9.1, 6 H), 7.37 ppm (*d*, *J* = 8.8, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): *d* = 14.01, 22.65, 26.77, 27.16, 31.67, 50.95, 72.01, 74.85, 80.61, 83.89, 106.69, 111.12, 117.25, 124.02, 133.54, 133.97, 146.72, 148.50 ppm; IR (neat): $\tilde{n}$ = 2924*m*, 2853*m*, 2201*m*, 2127*w*, 1567*s*, 1520*m*, 1499*s*, 1464*m*, 1402*m*, 1365*m*, 1315*s*, 1286*s*, 1172*s*, 1105*m*, 983*w*, 887*w*, 829*m*, 809*s* cm^{-1}; UV/Vis (CH_2Cl_2): l_{max} (*e*) = 287 (40600), 343 (90600), 387 (sh, 166000), 410 nm (200000); HR-MALDI-MS (DCTB): *m*/*z*: 1166.8096 ($[M]^+$, $C_{84}H_{102}N_4^+$, calc. 1166.8104); Anal. calc. for $C_{84}H_{102}N_4$ (1167.76): C 86.40, H 8.80, N 4.80; found: C 86.12, H 8.56, N 4.82.

Table 1SI: Electrochemical data of donor-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs) **1**–**3** and **5**–**9** observed by cyclic voltammetry (CV) and rotating disk voltammetry (RDV) in CH_2Cl_2 (+ 0.1 M nBu$_4$NPF$_6$). All potentials are given *vs.* ferricinium/ferrocene (Fc^+/Fc) couple used as internal standard.

	CV			RDV	
	$E°$ [V][a]	ΔE_p [mV][b]	E_p [V][c]	$E_{1/2}$ [V][d]	Slope [mV][e]
1[3]	–0.56	90		–0.60 (1e$^-$)	70
	–1.21	90		–1.30 (1e$^-$)	80
2[3]	+0.86	80		+0.87 (1e$^-$)	70
	–0.69	80		–0.70 (1e$^-$)	70
	–1.26	90		–1.38 (1e$^-$)	140
3[3]	+0.90	100		[f]	
	+0.72	90		+0.76 (1e$^-$)	75
	–0.89	90		–0.91 (1e$^-$)	80
	–1.18	90		–1.26 (1e$^-$)	90
5[2]	+0.88	90		+0.87 (3e$^-$)	60
	–0.67	160		–0.73 (3e$^-$)	120
	–1.13	180		–1.28 (3e$^-$)	150
6	+0.88	60		+0.91 (4e$^-$)	60
	–0.50	60		[g]	
	–0.66	60		[g]	
	–0.81	60		[g]	
	–0.85	60		[g]	
	–1.22	150		[g]	
7[2]	+0.95	100		+0.96 (3e$^-$)	70
			+0.80	+0.81 (2e$^-$)	70
	+0.61	115		+0.65 (2e$^-$)	60
	+0.40	110		+0.41 (2e$^-$)	70
	–1.12				
	–1.22			–1.40 (6e$^-$)	300
	–1.35				
	–1.40				
	–1.48				
	–1.55				
8	+1.00	60		+1.02 (1e$^-$)	60
	+0.88	80		+0.89 (3e$^-$)	70
	–0.72	155		–0.77 (3e$^-$)	100
	–1.12	120		–1.15 (3e$^-$)	80
9	+0.89	60		+0.90 (6e$^-$)	50
	+0.75	70		[h] (1e$^-$)	
	–0.68	120		–0.72 (6e$^-$)	100
	–1.08	130		–1.14 (6e$^-$)	120

[a] $E° = (E_{pc}+E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] $\Delta E_p = E_{ox}–E_{red}$, where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively. [c] E_p = irreversible peak potential. [d] $E_{1/2}$ = half-wave potential. [e] Slope = slope of the linearized plot of E versus $\log[I/(I_{lim}–I)]$, where I_{lim} is the limiting current and I the current. [f] Unresolved waves. [g] Unresolved spread-out wave. [h] Small-amplitude oxidation wave.

a) HOMO ($\mathbf{2}^{\bullet+}$) b) LUMO ($\mathbf{2}^{\bullet-}$)

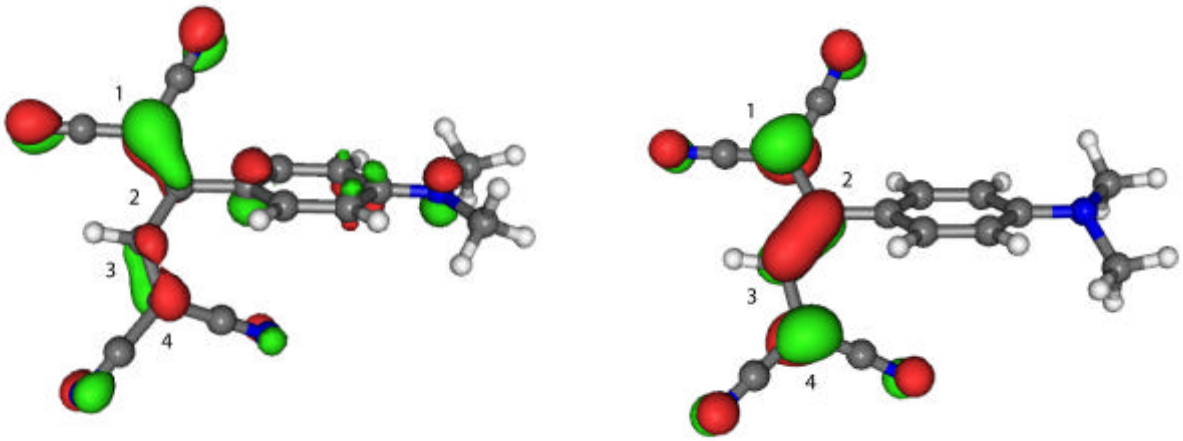


Figure 1SI: Optimized B3LYP/6-31g(d) geometry of $\mathbf{2}^{\bullet+}$ (a) and $\mathbf{2}^{\bullet-}$ (b) with overlaid molecular orbitals.

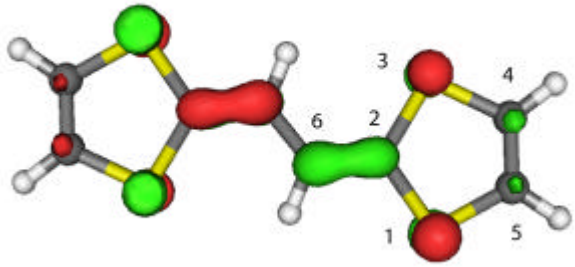


Figure 2SI: Optimized B3LYP/6-31g(d) geometry of **14** with overlaid HOMO.

References

[1] D. L. Mattern, *J. Org. Chem.* **1983**, *48*, 4772–4773.

[2] M. Kivala, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Angew. Chem.* **2007**, *119*, 6473–6477; *Angew. Chem. Int. Ed.* **2007**, *46*, 6357–6360.

[3] T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 1889–1905.