

Electronic Supplementary Information

A new class of organic donor-acceptor molecules with large third-order optical nonlinearities

Tsuyoshi Michinobu,^a Joshua C. May,^b Jin H. Lim,^b Corinne Boudon,^c Jean-Paul Gisselbrecht,^c Paul Seiler,^a Maurice Gross,^c Ivan Biaggio*^b and François Diederich*^a

^a *Laboratorium für Organische Chemie, ETH-Hönggerberg, CH-8093 Zürich, Switzerland.*

E-mail: diederich@org.chem.ethz.ch

^b *Center of Optical Technologies and Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.*

^c *Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, UMR 7512, C.N.R.S., Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France.*

Synthesis (ESI)

Synthesis of **1**: A solution of TCNE (176 mg, 1.37 mmol) in C₆H₆ (15 ml) was added to **4** (200 mg, 1.38 mmol) under nitrogen. The mixture was stirred at r.t. for 2.5 h. Evaporation and the subsequent column chromatography (SiO₂, CH₂Cl₂) afforded **1** (364 mg, 97%) as a purple solid, mp 144–145 °C; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 343 (10200), 481 (7000), 570 (4900); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3028, 2921, 2212, 1600, 1486, 1435, 1379, 1346, 1294, 1212, 1172, 942, 821; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 3.16 (6 H, s), 6.75 (2 H, d, *J* 9), 7.51 (2 H, d, *J* 9), 8.02 (1 H, s); $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$ 40.26, 77.98, 97.19, 109.06, 111.51, 112.10, 113.13, 113.74, 117.66, 132.11, 154.32, 156.67, 158.81; HR-EI-MS calcd for C₁₆H₁₁N₅⁺ (*M*⁺): 273.1014; found 272.0958, 273.1033; EA calcd for C₁₆H₁₁N₅ (273.29): C 70.32, H 4.06, N 25.63; found: C 70.13, H 4.08, N 25.35%.

Synthesis of **2**: A solution of TCNE (114 mg, 0.890 mmol) in C₆H₆ (15 ml) was added to **5** (257 mg, 0.891 mmol) under nitrogen. The mixture was stirred at r.t. for 2 h. Evaporation and the subsequent column chromatography (SiO₂, CH₂Cl₂) afforded **2** (354 mg, 96%) as a black solid, mp 191–193 °C; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 279 (13800), 430 (sh, 20800), 464 (sh, 25600), 526 (38100); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2917, 2217, 2122, 1598, 1538, 1479, 1435, 1372, 1329, 1295, 1210, 1171, 1113, 1063, 941, 808; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 3.10 (6 H, s), 3.15 (6 H, s), 6.64 (2 H, d, *J* 9), 6.72 (2 H, d, *J* 9), 7.48 (2 H, d, *J* 9), 7.82 (2 H, d, *J* 9); $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$ 40.29, 40.33, 74.38, 87.80, 90.42, 105.39, 111.71, 111.97, 112.12, 112.87, 113.55, 114.77, 117.93, 125.76, 132.70, 136.28, 150.15, 153.22, 154.53, 161.68; HR-ESI-MS calcd for C₂₆H₂₁N₆⁺ (*MH*⁺), C₂₆H₂₀N₆Na⁺ (*MNa*⁺): 417.1828, 439.1647; found 417.1822, 439.1637; EA calcd for C₂₆H₂₀N₆ (416.48): C 74.98, H 4.84, N 20.18; found: C 74.98, H 4.90, N 20.12%.

Synthesis of **3**: A solution of TCNE (24 mg, 0.19 mmol) in THF (2.0 ml) was added to a solution of **6** (50 mg, 0.19 mmol) in THF (5.0 ml) under argon. The mixture was stirred at

r.t. for 1 h. The solution was evaporated and passed through a plug (SiO₂, CH₂Cl₂) to afford **3** (76 mg, 100%) as a metallic red solid, mp 273.5–274.6 °C; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 278 (10400), 311 (sh, 5100), 323 (sh, 3400), 390 (sh, 17900), 470 (55000); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3076, 2921, 2853, 2206, 1597, 1455, 1428, 1377, 1353, 1322, 1286, 1168, 1062, 942, 818; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 3.14 (12 H, s), 6.69 (4 H, d, *J* 9), 7.79 (4 H, d, *J* 9); $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$ 40.14, 74.81, 111.85, 113.38, 114.59, 118.79, 132.44, 154.01, 165.38; HR-ESI-MS calcd for C₂₄H₂₁N₆⁺ (*MH*⁺), C₂₄H₂₀N₆Na⁺ (*MNa*⁺): 393.1828, 415.1647; found 393.1822, 415.1635; EA calcd for C₂₄H₂₀N₆ (392.46): C 73.45, H 5.14, N 21.41; found: C 70.99, H 5.18, N 20.00%.

Synthesis of **7**: To a solution of **8** (100 mg, 0.577 mmol) and CH₂(CN)₂ (57 mg, 0.86 mmol) in CH₂Cl₂ (2.0 ml), Al₂O₃ (activity II-III; 259 mg) was added. After refluxing for 50 min, the mixture was passed through a plug (SiO₂, CH₂Cl₂) and the filtrate was evaporated to yield **7** (111 mg, 87%) as a red solid, mp 130.3–131.4 °C; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 275 (10900), 306 (sh, 8600), 327 (sh, 4200), 477 (44100); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2913, 2221, 2135, 1607, 1549, 1373, 1336, 1233, 1190, 1171, 1062, 1037, 997, 943, 907, 809; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 3.09 (6 H, s), 6.65 (2 H, d, *J* 9), 7.10 (1 H, s), 7.48 (2 H, d, *J* 9); $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$ 40.22, 87.91, 88.64, 105.76, 111.88, 112.66, 113.89, 122.07, 135.80, 141.33, 152.74; ESI-MS calcd for C₁₄H₁₂N₃⁺ (*MH*⁺): 222.1; found 222.4; EA calcd for C₁₄H₁₁N₃ (221.26): C 76.00, H 5.01, N 18.99; found: C 75.79, H 5.16, N 18.88%.

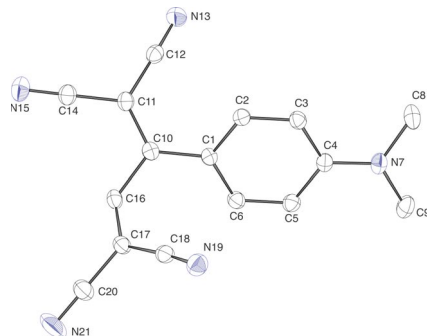
Electrochemistry (ESI)

Electrochemical investigations on a glassy carbon working electrode in CH_2Cl_2 containing 0.1M Bu_4NPF_6 as supporting electrolyte gave reduction and oxidation steps for all species. All oxidation steps correspond to electron transfers on the DMA moieties, whereas the reductions occur on the cyano-containing acceptor moieties.

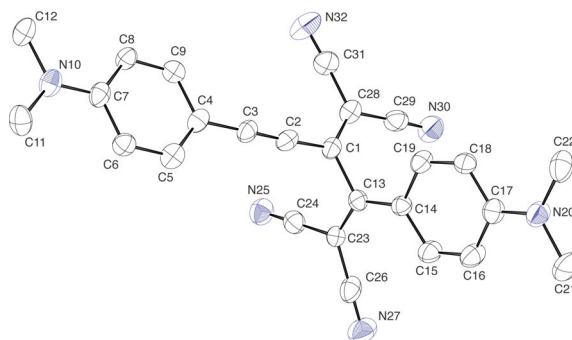
Experimental: The electrochemical experiments were carried out at 20 °C in CH_2Cl_2 containing 0.1M Bu_4NPF_6 in a classical three-electrode cell. CH_2Cl_2 was purchased spectroscopic grade from Merck, dried over molecular sieves (4 Å) and stored under argon prior to use. Bu_4NPF_6 was purchased electrochemical grade from Fluka and used as received. The working electrode was a glassy carbon disk electrode (2 mm in diameter) used either motionless for cyclic voltammetry (CV) (0.1 to 10 V s^{-1}) or as rotating-disk electrode for rotating-disk voltammetry (RDV). The auxiliary electrode was a platinum wire, and the reference electrode was an aqueous Ag/AgCl electrode. All potentials are referenced to the ferricinium/ferrocene (Fc^+/Fc) couple used as an internal standard and are uncorrected from ohmic drop. The accessible range of potentials on the glassy carbon electrode was +1.4 to -2.4 V versus Fc^+/Fc in CH_2Cl_2 . The electrochemical cell was connected to a computerized multipurpose electrochemical device AUTOLAB (Eco Chemie BV, Utrecht, The Netherlands) controlled by the GPES software running on a personal computer.

X-ray crystal data (ESI)

Fig. 1(ESI). Crystal data of **1**, **2**, **3** and **7**.

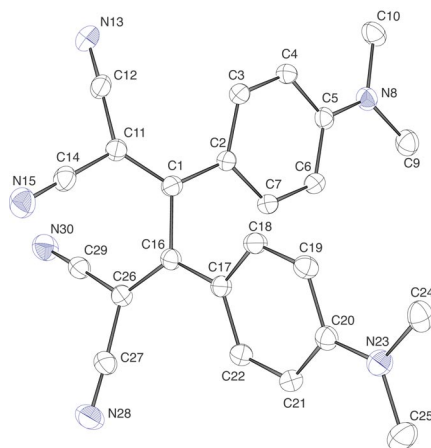


Selected bond lengths (Å) and angles (°) for one of the two different molecules in the unit cell: C1'–C2' 1.401(2), C1'–C6' 1.404(2), C1'–C10' 1.459(2), C2'–C3' 1.375(2), C3'–C4' 1.416(2), C4'–N7' 1.363(2), C4'–C5' 1.411(2), C5'–C6' 1.378(2), C10'–C11' 1.372(2), C10'–C16' 1.461(2), C16'–C17' 1.345(2), C11'–C10'–C1' 122.39(12), C12'–C11'–C14' 115.17(12), C17'–C16'–C10' 124.93(12), C18'–C17'–C20' 114.21(13).

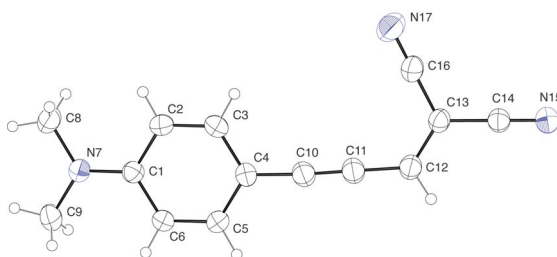


Selected bond lengths (Å) and angles (°): C1–C2 1.396(12), C1–C13 1.514(11), C2–C3 1.178(11), C3–C4 1.431(12), C4–C5 1.392(12), C4–C9 1.416(12), C5–C6 1.358(11), C6–C7 1.409(11), C7–N10 1.371(10), C7–C8 1.422(11), C8–C9 1.349(10), C13–C14 1.431(10), C14–C15 1.394(11), C14–C19 1.407(10), C15–C16 1.347(11), C16–C17 1.401(11), C17–N20 1.335(10), C17–C18 1.395(11), C18–C19 1.364(10), C28–C1–C13 120.5(7), C3–C2–C1 175.2(8), C2–C3–C4 178.8(8), C23–C13–C1 113.3(6), C24–C23–C26

114.0(7), C31–C28–C29 116.6(8). The geometry of **2** is *ca.* 4 times less precise than that obtained for the other molecules.

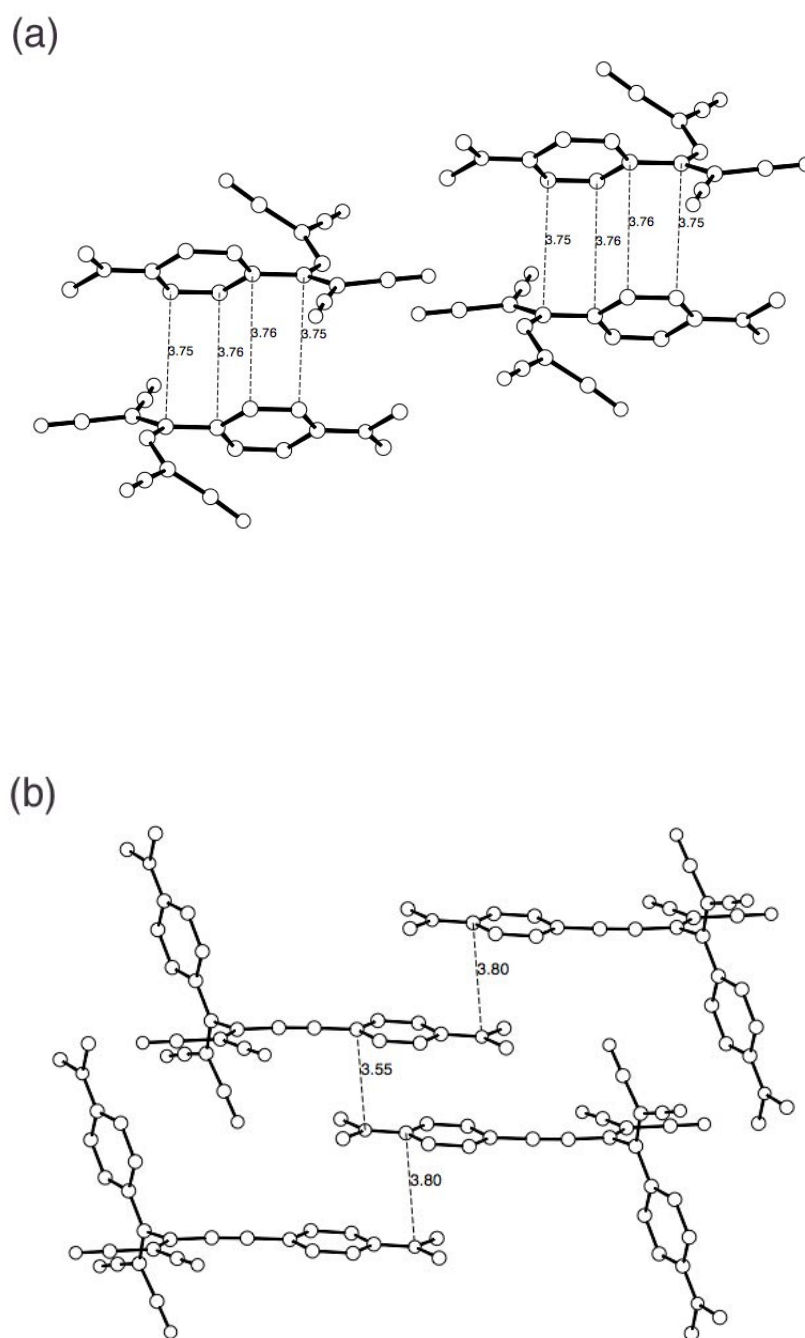


Selected bond lengths (Å) and angles (°): C1–C11 1.388(2), C1–C2 1.438(2), C1–C16 1.508(2), C2–C7 1.411(2), C2–C3 1.415(3), C3–C4 1.364(3), C4–C5 1.425(3), C5–N8 1.357(2), C5–C6 1.413(3), C6–C7 1.365(3), C11–C1–C2 125.61(16), C1–C11–C14 120.96(17).

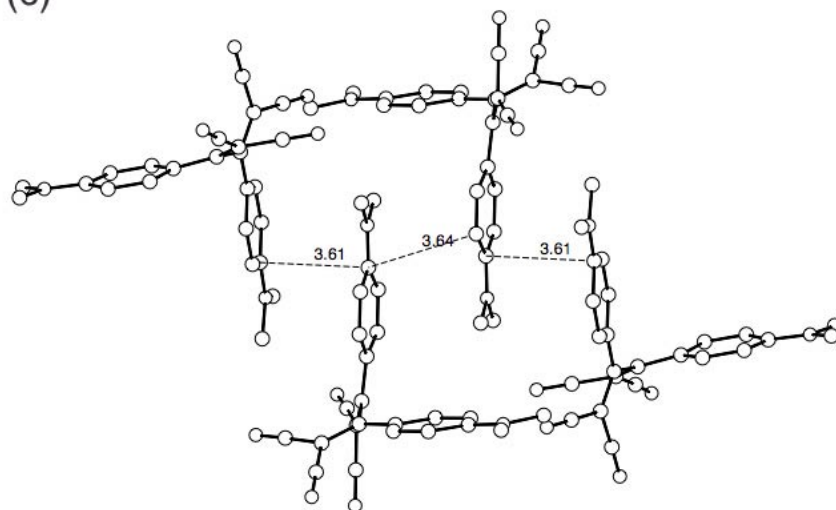


Selected bond lengths (Å) and angles (°): C1–N7 1.361(3), C1–C2 1.402(3), C1–C6 1.406(3), C2–C3 1.362(3), C3–C4 1.388(3), C4–C5 1.392(3), C4–C10 1.415(3), C5–C6 1.366(3), C10–C11 1.212(3), C11–C12 1.387(3), C12–C13 1.353(3), C11–C10–C4 176.4(2), C10–C11–C12 178.2(2), C14–C13–C16 116.13(19).

Fig. 2(ESI). Crystal packings of **1** (a), **2** (b), **3** (c) and **7** (d).



(c)



(d)

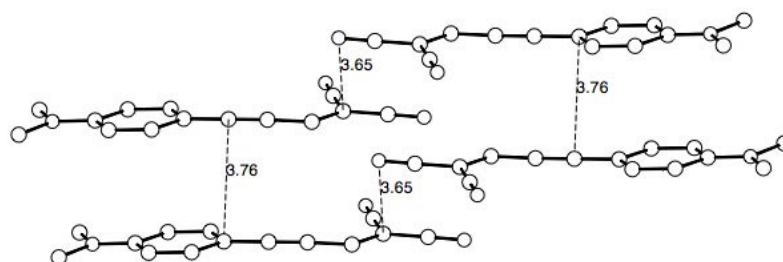
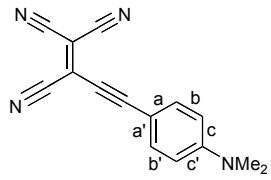
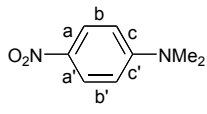


Table 1(ESI). Comparison of quinoid character: $\delta r = (((a + a')/2 - (b + b')/2) + ((c + c')/2 - (b + b')/2))/2$.

	$\delta r / \text{Å}$	Ref.
	0.037	1
	0.029	2
1	0.036	
3	0.050	
7	0.033	

1. N. N. P. Moonen, R. Gist, C. Boudon, J.-P. Gisselbrecht, P. Seiler, T. Kawai, A. Kinoshita, M. Gross, M. Irie and F. Diederich, *Org. Biomol. Chem.*, 2003, **1**, 2032.
2. O. Y. Borbulevych, R. D. Clark, A. Romero, L. Tan, M. Y. Antipin, V. N. Nesterov, B. H. Cardelino, C. E. Moore, M. Sanghadasa and T. V. Timofeeva, *J. Mol. Struct.*, 2002, **604**, 73.

Table 2(ESI). Cyclic voltammetry and rotating-disk voltammetry data in CH₂Cl₂ (+ 0.1M Bu₄NPF₆): potentials vs. Fc⁺/Fc. Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl. Scan rate: 0.1 V s⁻¹.

	Cyclic Voltammetry			Rotating-disk Voltammetry	
	E°/V^a	$\Delta E_p/mV$	E_{pc}/V^b	$E_{1/2}/V$	Slope /mV
1	+0.86	80		+0.87 (1e ⁻)	70
	-0.69	80		-0.70 (1e ⁻)	70
	-1.26	90		-1.38 (1e ⁻)	140
2	+0.90	100		c	
	+0.72	90		+0.76 (1e ⁻)	75
	-0.89	90		-0.91 (1e ⁻)	80
	-1.18	90		-1.26 (1e ⁻)	90
3	+0.91	d		+0.89 (2e ⁻)	125
	+0.86	90			
	-1.06	90		-1.08 (1e ⁻)	75
	-1.29	90		-1.36 (1e ⁻)	100
7	+0.66 ^e			+0.70 (1e ⁻)	70
			-1.50	-1.50 (1e ⁻)	100

^a $E^{\circ} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.

^b Irreversible peak potential.

^c The second oxidation was not well resolved.

^d Could not be determined due to the presence of a cathodic redissolution peak at scan rates lower than 1 V s⁻¹.

^e Scan rate: 2 V s⁻¹.