Supplementary Material

5-ARYLIDENETETRONATE AS A VERSATILE ELECTROPHORE FOR

PI-EXTENDED ELECTRON ACCEPTORS

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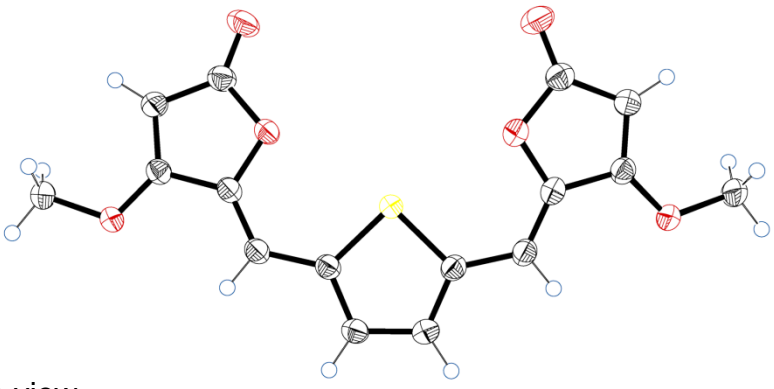
Crystal Data of **1b**

Empirical formula	$C_{16}H_{12}O_6S$
Formula weight	332.32
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.64087(8)
b/Å	27.0733(2)
c/Å	7.57532(8)
α/°	90
β/°	111.3145(12)
γ/°	90
Volume/Å^3	1459.87(3)
Z	4
ρ_{calc}g/cm^3	1.512
μ/mm^{-1}	2.258
F(000)	688.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.53 to 151.094
Index ranges	-9 ≤ h ≤ 9, -33 ≤ k ≤ 31, -5 ≤ l ≤ 9
Reflections collected	8589
Independent reflections	2940 [R_{int} = 0.0139, R_{sigma} = 0.0134]
Data/restraints/parameters	2940/0/210
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0839
Final R indexes [all data]	R_1 = 0.0316, wR_2 = 0.0845
Largest diff. peak/hole / e Å^{-3}	0.22/-0.28

top view



side view

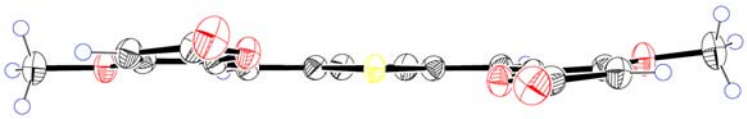
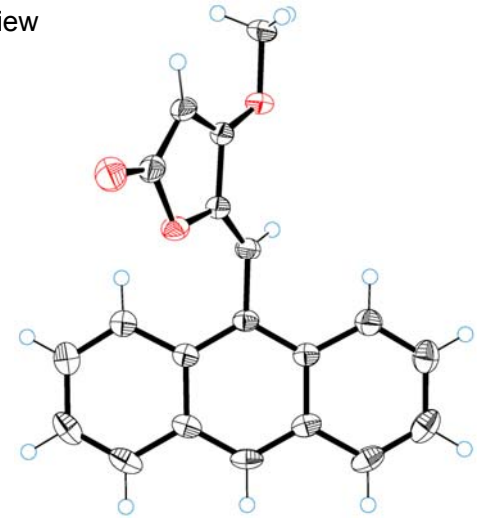


Figure S1. X-ray structure of **1b**

Crystal Data of **2a**

Empirical formula	$C_{20}H_{14}O_3$
Formula weight	302.31
Temperature/K	150
Crystal system	monoclinic
Space group	I2/a
a/Å	19.8997(3)
b/Å	3.99030(6)
c/Å	36.7757(5)
α/°	90
β/°	90.5811(12)
γ/°	90
Volume/Å^3	2920.05(7)
Z	8
ρ_{calc}g/cm^3	1.375
μ/mm^{-1}	0.745
F(000)	1264.0
Crystal size/mm^3	0.8 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.806 to 151.91
Index ranges	-24 ≤ h ≤ 23, -1 ≤ k ≤ 4, -46 ≤ l ≤ 43
Reflections collected	7722
Independent reflections	2932 [R_{int} = 0.0122, R_{sigma} = 0.0142]
Data/restraints/parameters	2932/0/209
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0351, wR_2 = 0.0970
Final R indexes [all data]	R_1 = 0.0366, wR_2 = 0.0984
Largest diff. peak/hole / e Å^{-3}	0.19/-0.18

top view



side view

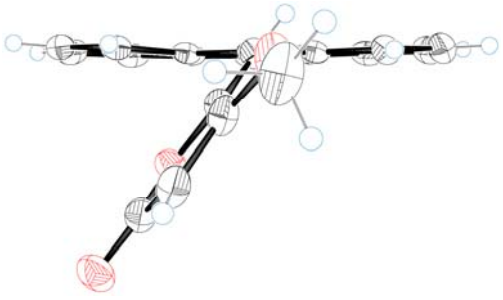


Figure S2. X-ray structure of **2a**

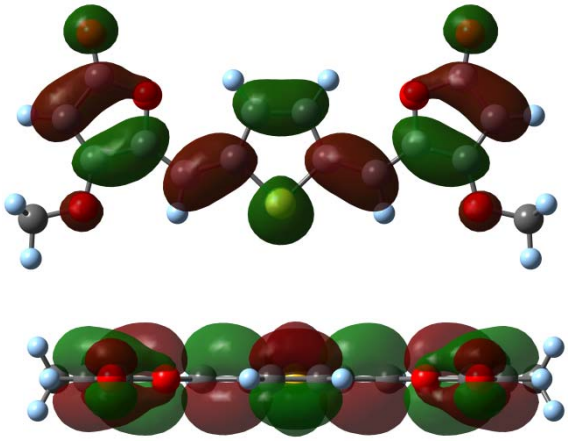
Table S1. The energy and MO levels in **1b** for various geometries and stereoisomers

	Z,Z-anti	***Z,Z-syn***	***E,E-anti***	***E,E-syn***
B3LYP/6-31G(d,p)				
energy (kcal/mol)	-920200.7757	-920200.4701	-920190.2141	-920190.9382
ΔE (kcal/mol)	**0.00**	**0.31**	**10.56**	**9.84**
LUMO (a.u.)	-0.09377	-0.09000	-0.10060	-0.10131
HOMO (a.u.)	-0.19819	-0.19476	-0.20375	-0.20475
LUMO (eV)	**-2.55**	**-2.45**	**-2.74**	**-2.76**
HOMO (eV)	**-5.39**	**-5.30**	**-5.54**	**-5.57**
HOMO-LUMO gap (eV)	2.84	2.85	2.81	2.81
HOMO-LUMO gap (nm)	436	435	442	440

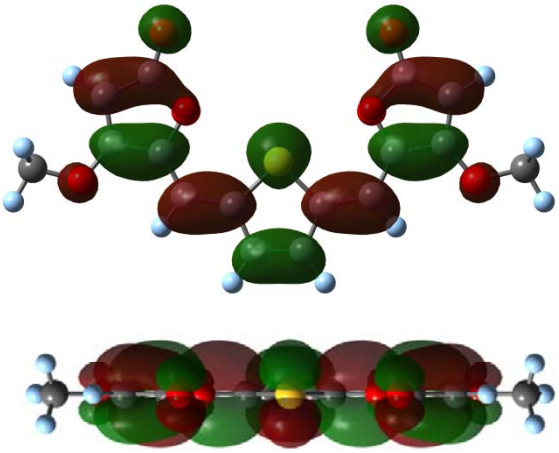
a) *Z,Z-anti*-**1b**

b) *Z,Z-syn*-**1b**

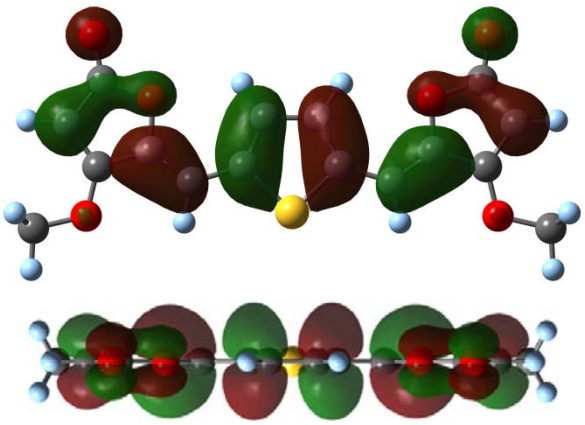
LUMO



LUMO



HOMO



HOMO

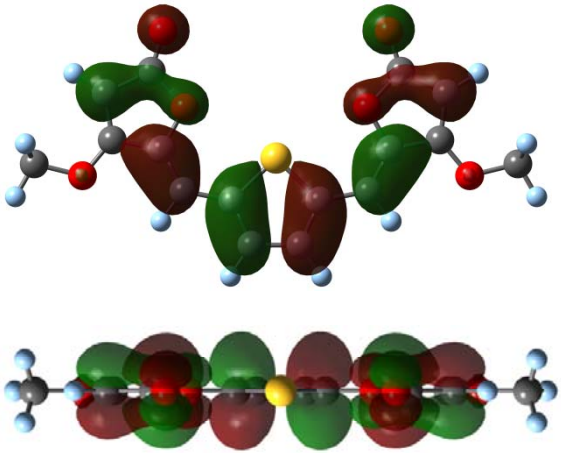


Figure S3. HOMO and LUMO of (a) *Z,Z-anti*-**1b** and (b) *Z,Z-syn*-**1b**

(ref. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.)