Electronic Supplementary Information

Facile Synthesis and Properties of Dithieno[3,2-*b*:2',3'-*d*]arsoles

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Contents:

1. NMR spectra

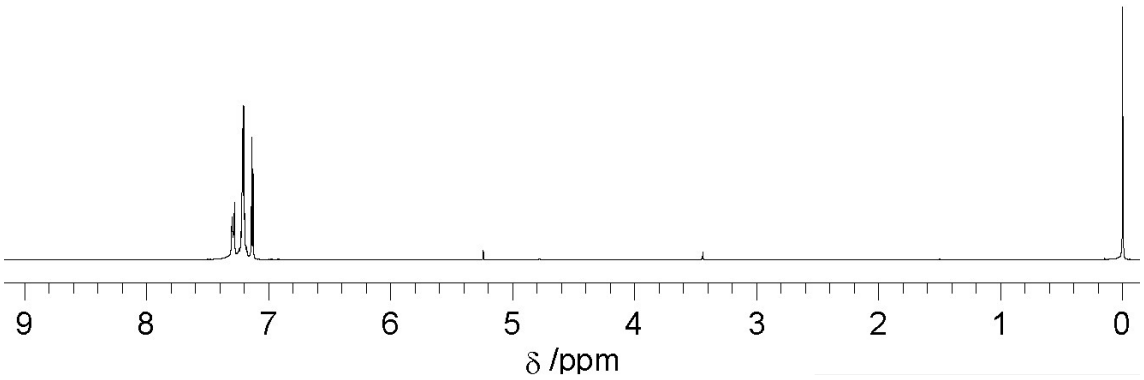


Fig. S1 ^{1}H NMR spectrum (400 MHz) of **3** in $CDCl_3$.

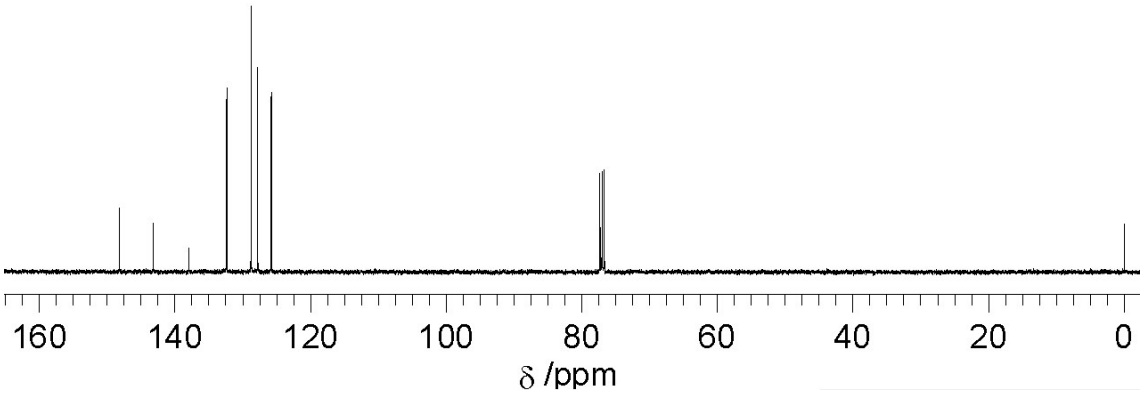


Fig. S2 ^{13}C NMR spectrum (100 MHz) of **3** in $CDCl_3$.

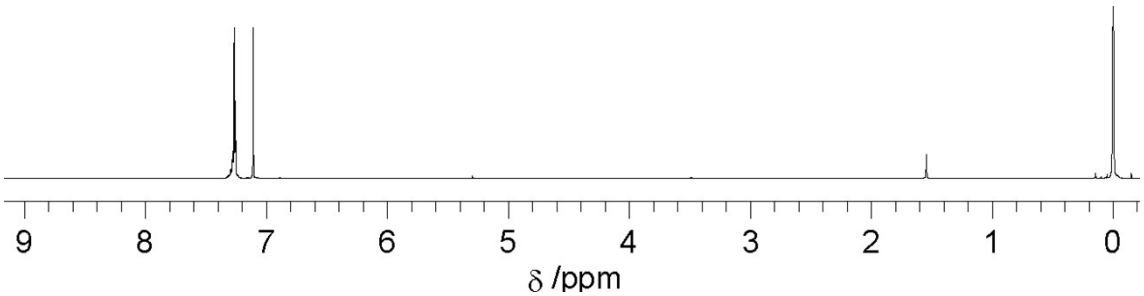


Fig. S3 ^{1}H NMR spectrum (400 MHz) of **4** in $CDCl_3$.

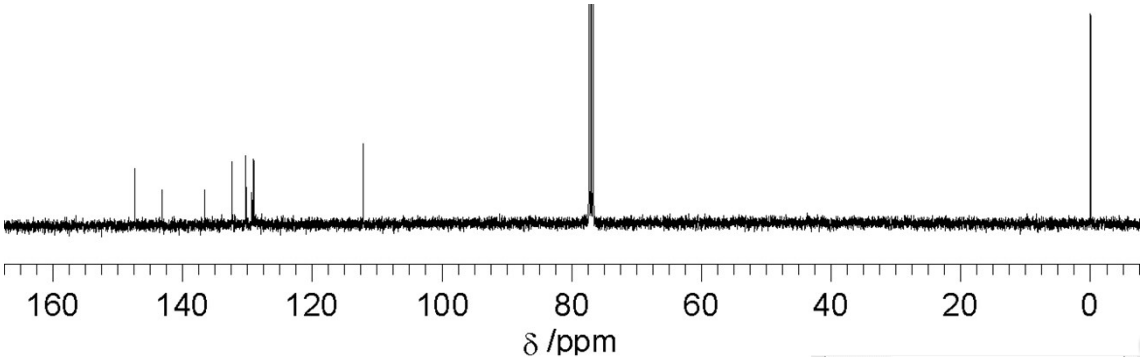


Fig. S4 ^{13}C NMR spectrum (100 MHz) of **4** in $CDCl_3$.

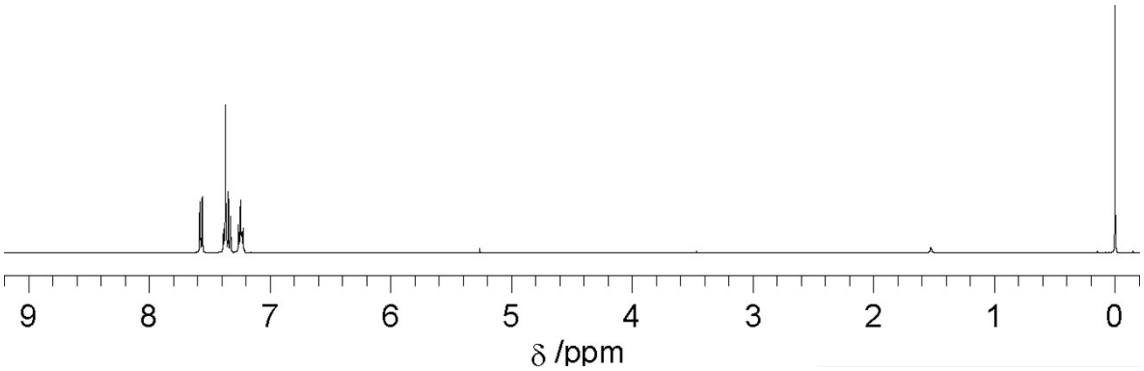


Fig. S5 ^{1}H NMR spectrum (400 MHz) of **5** in $CDCl_3$.

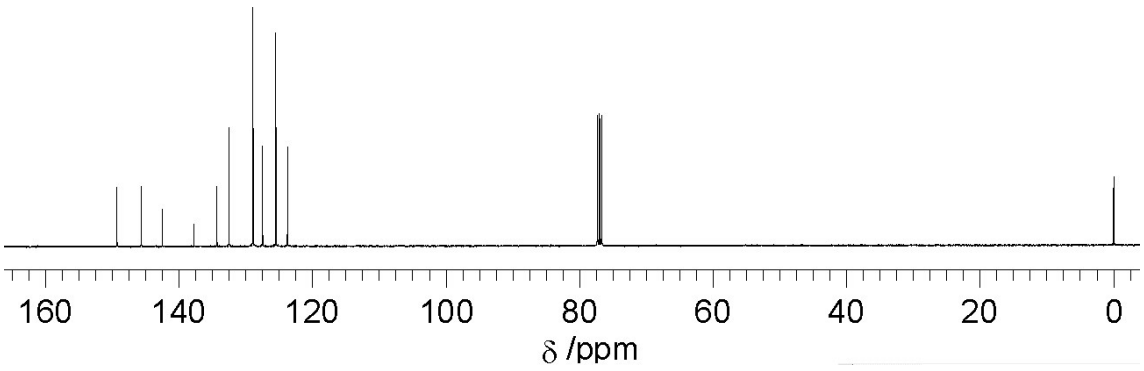


Fig. S6 ^{13}C NMR spectrum (100 MHz) of **5** in $CDCl_3$.

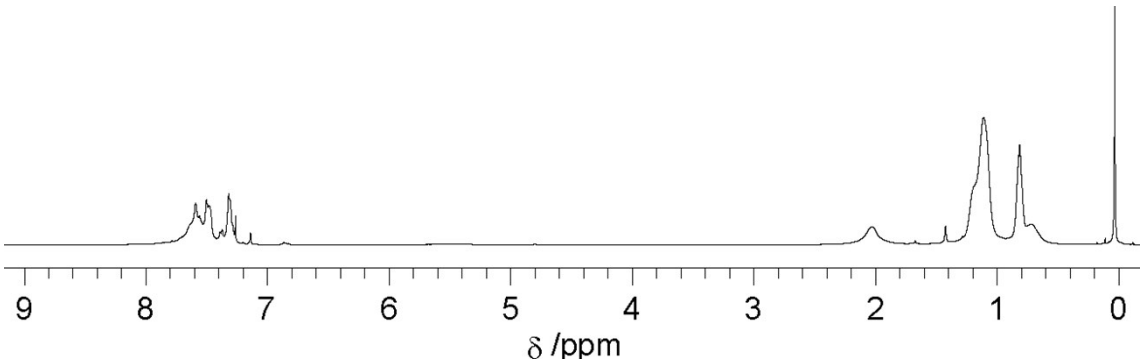


Fig. S7 ^{1}H NMR spectrum (400 MHz) of **6** in $CDCl_3$.

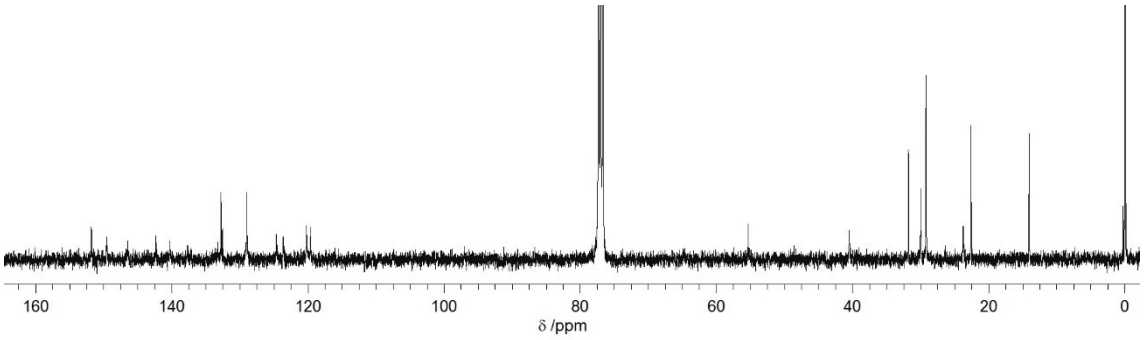
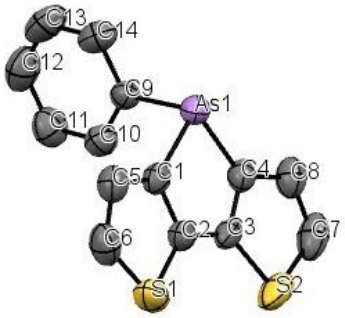


Fig. S8 ^{13}C NMR spectrum (100 MHz) of **6** in $CDCl_3$.

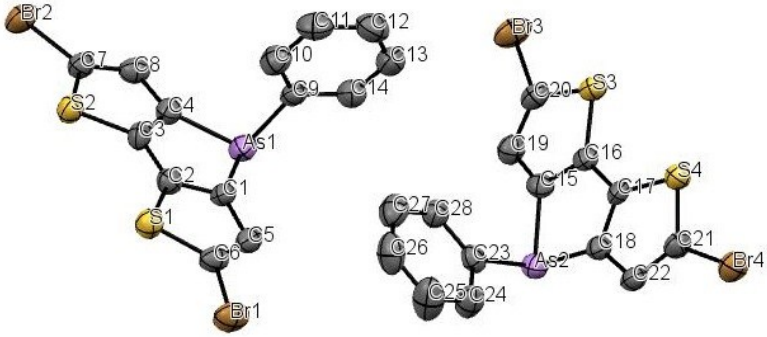
2. Crystallographic data

Table S1. ORTEP drawing (ellipsoids at 50% probability), selected angles (deg) and distances (Å) of **3**.



interplanar angle (°)		angle (°)	
As(1)C(1)C(2)C(3)C(4)-S(1)C(2)C(1)C(5)C(6)	1.94	C(1)-As(1)-C(4)	85.4(2)
		C(1)-As(1)-C(9)	97.2(2)
As(1)C(1)C(2)C(3)C(4)-S(2)C(3)C(4)C(8)C(7)	5.50	C(4)-As(1)-C(9)	101.3(2)
		C(2)-S(1)-C(6)	91.1(2)
distance (Å)		C(3)-S(2)-C(7)	90.6(2)
As(1)-C(1)	1.956(4)	As(1)-C(1)-C(2)	111.0(3)
As(1)-C(4)	1.951(4)	As(1)-C(1)-C(5)	136.2(3)
As(1)-C(9)	1.965(4)	C(2)-C(1)-C(5)	112.6(3)
S(1)-C(2)	1.726(4)	S(1)-C(2)-C(1)	111.4(3)
S(1)-C(6)	1.718(5)	S(1)-C(2)-C(3)	132.6(3)
S(2)-C(3)	1.721(4)	C(1)-C(2)-C(3)	116.0(3)
S(2)-C(7)	1.726(5)	S(2)-C(3)-C(2)	131.7(3)
C(1)-C(2)	1.380(5)	S(2)-C(3)-C(4)	112.1(3)
C(2)-C(3)	1.440(5)	C(2)-C(3)-C(4)	116.1(3)
C(3)-C(4)	1.375(5)	As(1)-C(4)-C(3)	111.4(3)
C(1)-C(5)	1.416(5)	As(1)-C(4)-C(8)	135.6(3)
C(5)-C(6)	1.359(6)		
C(4)-C(8)	1.427(5)		
C(7)-C(8)	1.352(6)		

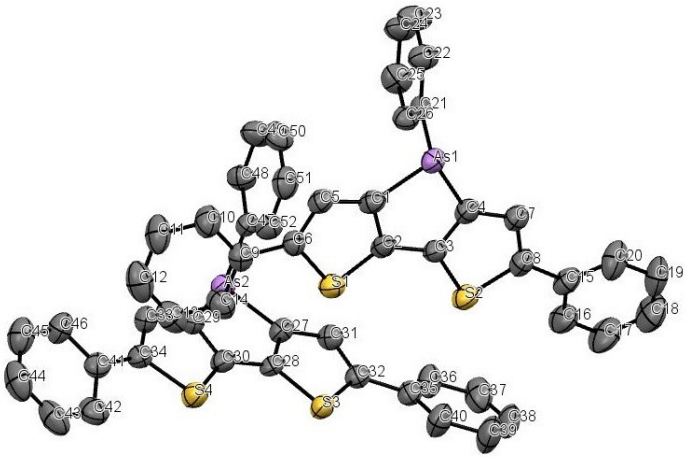
Table S2. ORTEP drawing (ellipsoids at 50% probability), selected angles (deg) and distances (Å) of **4**.



interplanar angle (°)		angle (°)	
As(1)C(1)C(2)C(3)C(4)-S(1)C(2)C(1)C(5)C(6)	1.35	C(1)-As(1)-C(4)	85.4(2)
		C(1)-As(1)-C(9)	96.3(2)
As(1)C(1)C(2)C(3)C(4)-S(2)C(3)C(4)C(8)C(7)	5.27	C(4)-As(1)-C(9)	100.8(2)
		C(15)-As(2)-C(18)	85.1(2)
As(2)C(15)C(16)C(17)C(18)-S(3)C(16)C(15)C(19)C(20)	1.07	C(15)-As(2)-C(23)	99.2(2)
		C(18)-As(2)-C(23)	96.3(2)
As(2)C(15)C(16)C(17)C(18)-S(4)C(17)C(18)C(22)C(21)	2.89	As(1)-C(1)-C(2)	111.9(4)
		C(1)-C(2)-C(3)	115.2(5)
distance (Å)		C(2)-C(3)-C(4)	116.1(5)
As(1)-C(1)	1.948(5)	As(1)-C(4)-C(3)	111.4(4)
As(1)-C(4)	1.946(6)	As(2)-C(15)-C(16)	110.8(4)
As(1)-C(9)	1.959(5)	C(15)-C(16)-C(17)	117.0(5)
As(2)-C(15)	1.952(5)	C(16)-C(17)-C(18)	115.6(5)
As(2)-C(18)	1.964(5)	As(2)-C(18)-C(17)	111.2(4)
As(2)-C(23)	1.970(5)	C(2)-S(1)-C(6)	89.3(3)
S(1)-C(2)	1.721(5)	C(3)-S(2)-C(7)	90.2(3)
S(1)-C(6)	1.721(7)	C(16)-S(3)-C(20)	90.3(3)
S(2)-C(3)	1.725(6)	C(17)-S(4)-C(21)	90.4(3)
S(2)-C(7)	1.723(6)		
S(3)-C(16)	1.725(5)		
S(3)-C(20)	1.727(6)		
S(4)-C(17)	1.712(5)		
S(4)-C(21)	1.724(6)		
C(1)-C(2)	1.375(8)		

C(3)-C(4)	1.377(7)
C(2)-C(3)	1.451(8)
C(15)-C(16)	1.371(6)
C(17)-C(18)	1.369(6)
C(16)-C(17)	1.434(8)

Table S3. ORTEP drawing (ellipsoids at 50% probability), selected angles (deg) and distances (Å) of **5**.



interplanar angle (°)		angle (°)	
As(1)C(1)C(2)C(3)C(4)-S(1)C(2)C(1)C(5)C(6)	3.04	C(1)-As(1)-C(4)	85.2(5)
		C(1)-As(1)-C(21)	99.1(4)
As(1)C(1)C(2)C(3)C(4)-S(2)C(3)C(4)C(7)C(8)	2.98	C(4)-As(1)-C(21)	99.4(5)
		C(27)-As(2)-C(29)	85.0(5)
As(2)C(27)C(28)C(30)C(29)-S(3)C(28)C(27)C(31)C(32)	1.79	C(27)-As(2)-C(47)	99.3(4)
		C(29)-As(2)-C(47)	98.4(5)
As(2)C(27)C(28)C(30)C(29)-S(4)C(30)C(29)C(33)C(34)	2.23	As(1)-C(1)-C(2)	111.4(8)
		C(1)-C(2)-C(3)	116(1)
distance (Å)		C(2)-C(3)-C(4)	116(1)
As(1)-C(1)	1.93(1)	As(1)-C(4)-C(3)	111.2(8)
As(1)-C(4)	1.94(1)	As(2)-C(27)-C(28)	111.8(8)
As(1)-C(21)	1.93(1)	C(27)-C(28)-C(30)	116(1)
As(2)-C(27)	1.929(9)	C(28)-C(30)-C(29)	116(1)
As(2)-C(29)	1.94(1)	As(2)-C(29)-C(30)	111.7(8)
As(2)-C(47)	1.95(1)	C(2)-S(1)-C(6)	91.1(5)
S(1)-C(2)	1.69(1)	C(3)-S(2)-C(8)	91.6(6)
S(1)-C(6)	1.730(9)	C(28)-S(3)-C(32)	91.1(5)
S(2)-C(3)	1.70(1)	C(30)-S(4)-C(34)	91.4(6)
S(2)-C(8)	1.72(1)	torsion angle (°)	
S(3)-C(28)	1.700(9)	S(1)-C(6)-C(9)-C(14)	6.74(2)
S(3)-C(32)	1.74(1)	S(2)-C(8)-C(15)-C(16)	15.43(2)
S(4)-C(30)	1.71(1)	S(3)-C(32)-C(35)-C(40)	20.99(2)

S(4)-C(34)	1.74(1)	S(4)-C(34)-C(41)-C(42)	15.40(2)
C(1)-C(2)	1.37(1)		
C(3)-C(4)	1.36(2)		
C(2)-C(3)	1.43(1)		
C(27)-C(28)	1.36(2)		
C(28)-C(30)	1.44(1)		
C(29)-C(30)	1.35(1)		
C(6)-C(9)	1.46(2)		
C(8)-C(15)	1.46(1)		
C(32)-C(35)	1.46(1)		
C(34)-C(41)	1.46(2)		

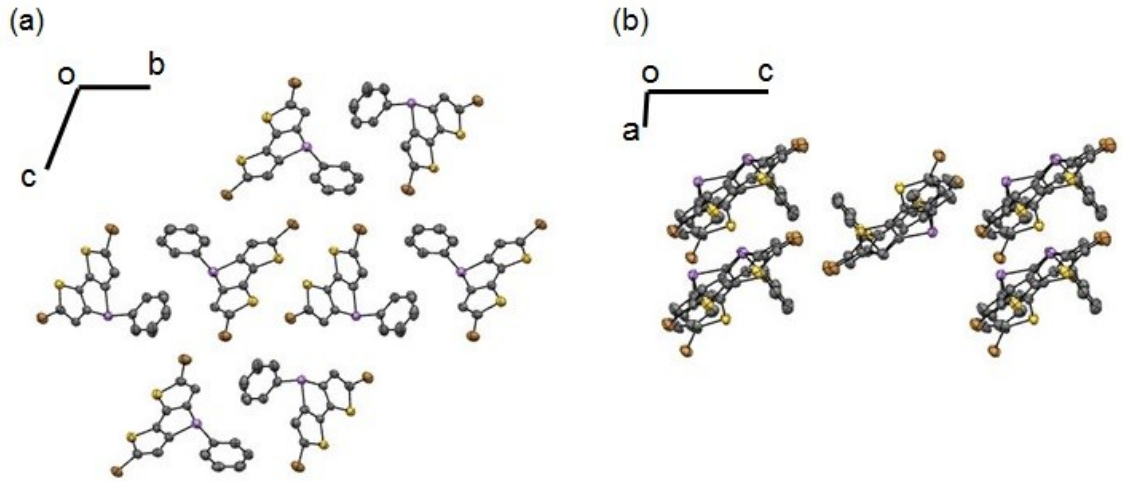


Fig. S9 Packing structures of **4** along (a) *a*-axis and (b) *b*-axis. Hydrogen atoms are omitted for clarity.

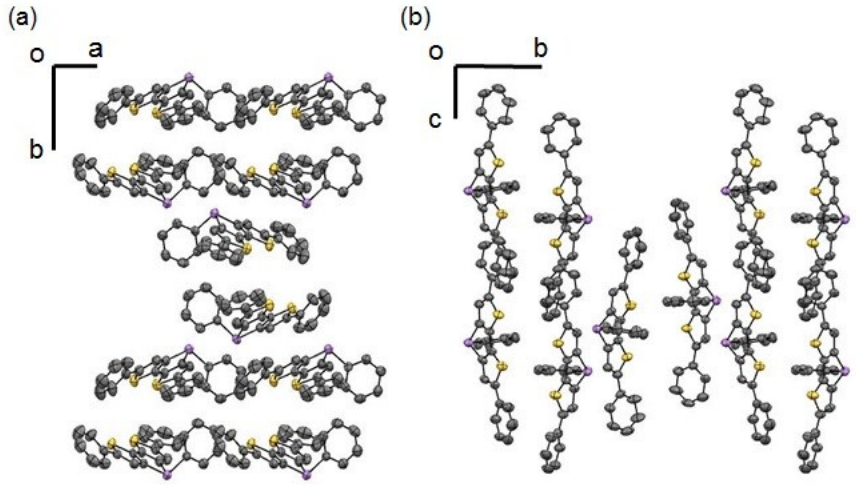


Fig. S10 Packing structures of **5** along (a) *c*-axis and (b) *a*-axis. Hydrogen atoms are omitted for clarity.

3. Optical properties

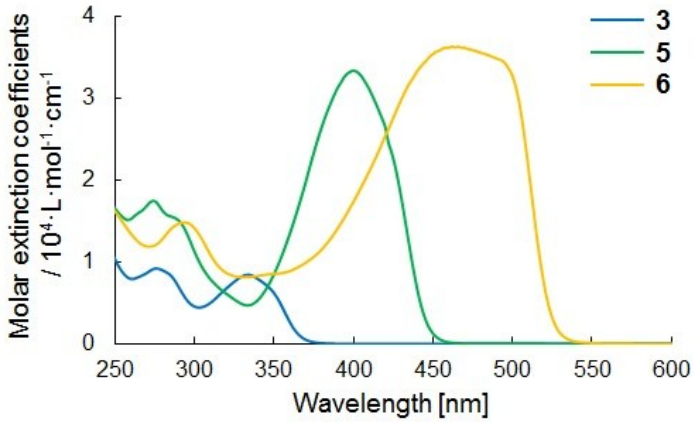


Fig. S11 UV-vis absorption spectra of **3**, **5** and **6** (1.0×10^{-4} M $CHCl_3$ solution).

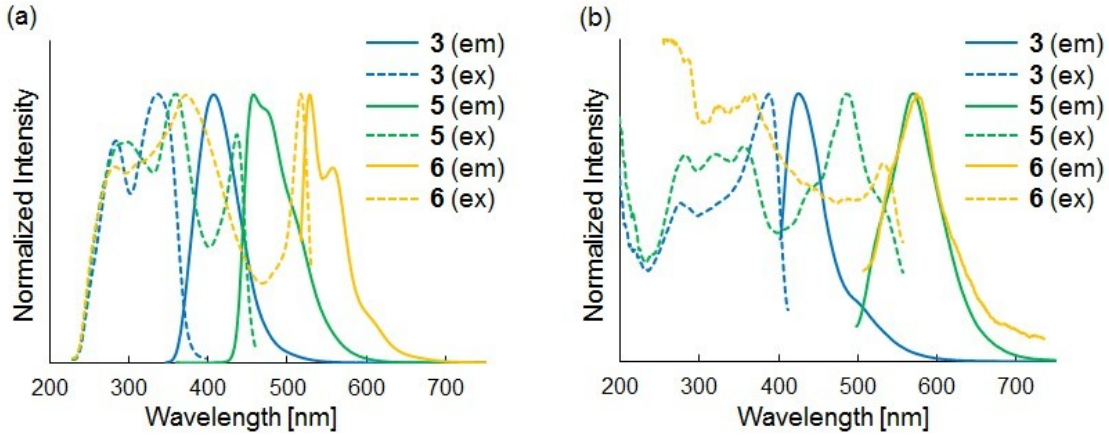


Fig. S12 PL and excitation spectra of **3**, **5** and **6** in (a) solutions (1.0×10^{-4} M in $CHCl_3$) and (b) solid states.

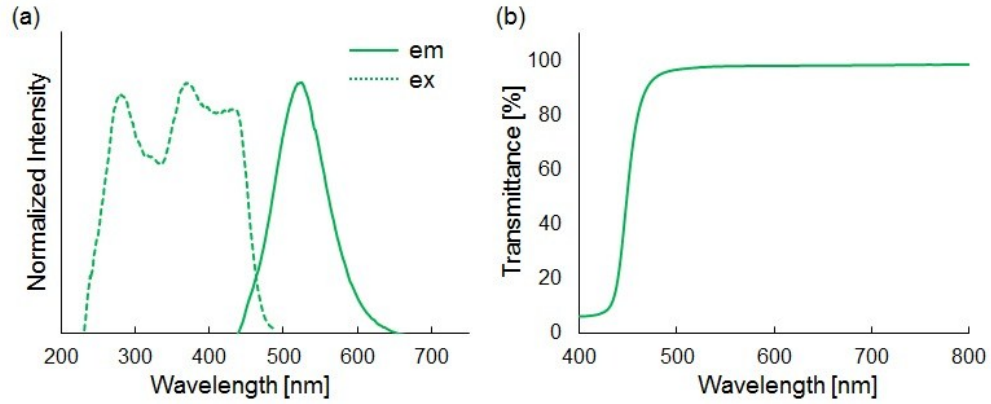


Fig. S13 (a) PL and excitation spectra and (b) transmission spectrum of **5**/PMMA film (10 wt%).

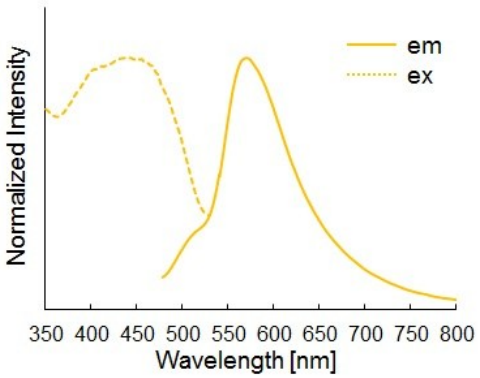


Fig. S14 (a) PL and excitation spectra and (b) transmission spectrum of **6**/PMMA film (10 wt%).

4. CV data

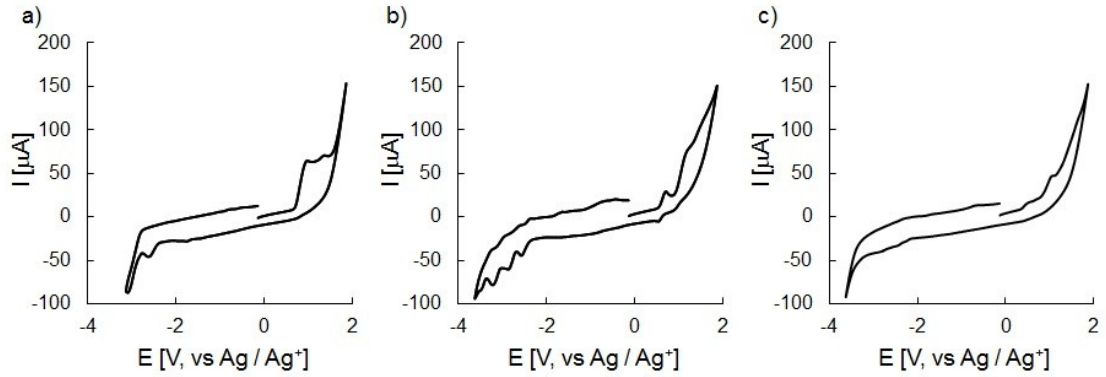


Fig. S15 Cyclic voltammograms of (a) **3** (b) **5**, and (c) **6** measured in THF solutions (c = 0.1 M) at the scan rate of 100 mV/s under N_2. The working electrode was a glassy carbon, the counter electrode was a platinum wire, and the reference electrode was an Ag^0 / Ag^+.

5. Theoretical calculations

Table S4. Atom coordinates and absolute energy level for **3** optimized in the S_0 state.

3 (S_0 state): E(RB3LYP) = -3569.10172537 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	33	0	-0.5332	-0.0001	-1.3449
2	16	0	2.8151	1.8926	0.7597
3	16	0	2.8151	-1.8925	0.7599
4	6	0	0.6125	1.3291	-0.4884
5	6	0	1.6913	0.7226	0.1353
6	6	0	1.6913	-0.7225	0.1353
7	6	0	0.6125	-1.3292	-0.4883
8	6	0	0.6973	2.749	-0.4755
9	6	0	1.8197	3.2009	0.1723
10	6	0	1.8198	-3.2008	0.1725
11	6	0	0.6974	-2.7491	-0.4754
12	6	0	-2.0826	0	-0.1376
13	6	0	-1.9656	0.0002	1.2578
14	6	0	-3.1034	0.0003	2.0649
15	6	0	-4.3762	0.0001	1.482
16	6	0	-4.5029	-0.0002	0.0919
17	6	0	-3.3581	-0.0002	-0.7134
18	1	0	-0.0373	3.414	-0.9153
19	1	0	2.1312	4.2225	0.3426
20	1	0	2.1312	-4.2225	0.3429
21	1	0	-0.0372	-3.4141	-0.9152
22	1	0	-0.9817	0.0003	1.7182
23	1	0	-2.9996	0.0005	3.1465
24	1	0	-5.2626	0.0001	2.11
25	1	0	-5.4874	-0.0003	-0.3675
26	1	0	-3.4631	-0.0004	-1.7955

Table S5. Atom coordinates and absolute energy level for **5** optimized in the S_0 state.

5 (S_0 state): E(RB3LYP) = -4031.24967753 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	33	0	0.0035	1.566	-1.4191
2	16	0	1.8927	-1.9886	0.3241
3	16	0	-1.8905	-1.9816	0.3364
4	6	0	1.3288	0.3238	-0.7049
5	6	0	0.7218	-0.8129	-0.1904
6	6	0	-0.7189	-0.8137	-0.1913
7	6	0	-1.3251	0.3216	-0.709
8	6	0	2.7416	0.2412	-0.7022
9	6	0	3.2248	-0.9386	-0.1683
10	6	0	-3.2221	-0.9201	-0.1313
11	6	0	-2.7389	0.2534	-0.6801
12	6	0	-0.0036	2.9527	-0.0249
13	6	0	0.0009	2.6588	1.3437
14	6	0	-0.0065	3.6853	2.2882
15	6	0	-0.0173	5.0215	1.8707
16	6	0	-0.0216	5.3233	0.5076
17	6	0	-0.0152	4.2901	-0.4368
18	1	0	3.3946	1.0125	-1.094
19	6	0	4.6214	-1.3431	0.0239
20	6	0	-4.6173	-1.3275	0.0682
21	1	0	-3.3914	1.0505	-1.0174
22	1	0	0.0093	1.6246	1.6749
23	1	0	-0.0035	3.4458	3.3479
24	1	0	-0.0226	5.8215	2.6055
25	1	0	-0.0304	6.3582	0.1769
26	1	0	-0.0187	4.5302	-1.4972
27	6	0	5.6252	-0.3652	0.1764
28	6	0	5.0032	-2.6979	0.0696
29	6	0	6.3372	-3.0603	0.2544
30	6	0	6.9583	-0.7308	0.354
31	6	0	7.3235	-2.08	0.3935
32	1	0	4.2535	-3.4731	-0.0613
33	1	0	6.6067	-4.1123	0.2816
34	1	0	5.353	0.6855	0.1823
35	1	0	7.7133	0.0412	0.4735
36	1	0	8.362	-2.3633	0.5365
37	6	0	-4.9851	-2.2434	1.073
38	6	0	-5.6343	-0.8026	-0.7546
39	6	0	-6.9662	-1.1685	-0.5677
40	6	0	-6.3174	-2.6159	1.2507
41	6	0	-7.3165	-2.0785	0.4347
42	1	0	-5.374	-0.1217	-1.5588

43	1	0	-7.7314	-0.7519	-1.2165
44	1	0	-4.2256	-2.6505	1.7344
45	1	0	-6.5753	-3.3215	2.0352
46	1	0	-8.3538	-2.3671	0.5754