Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information for

Supermolecular Interactions Induced Fluorescent Organic Nanowires with High Quantum Yield Based on 9,10-Distyrylanthracene

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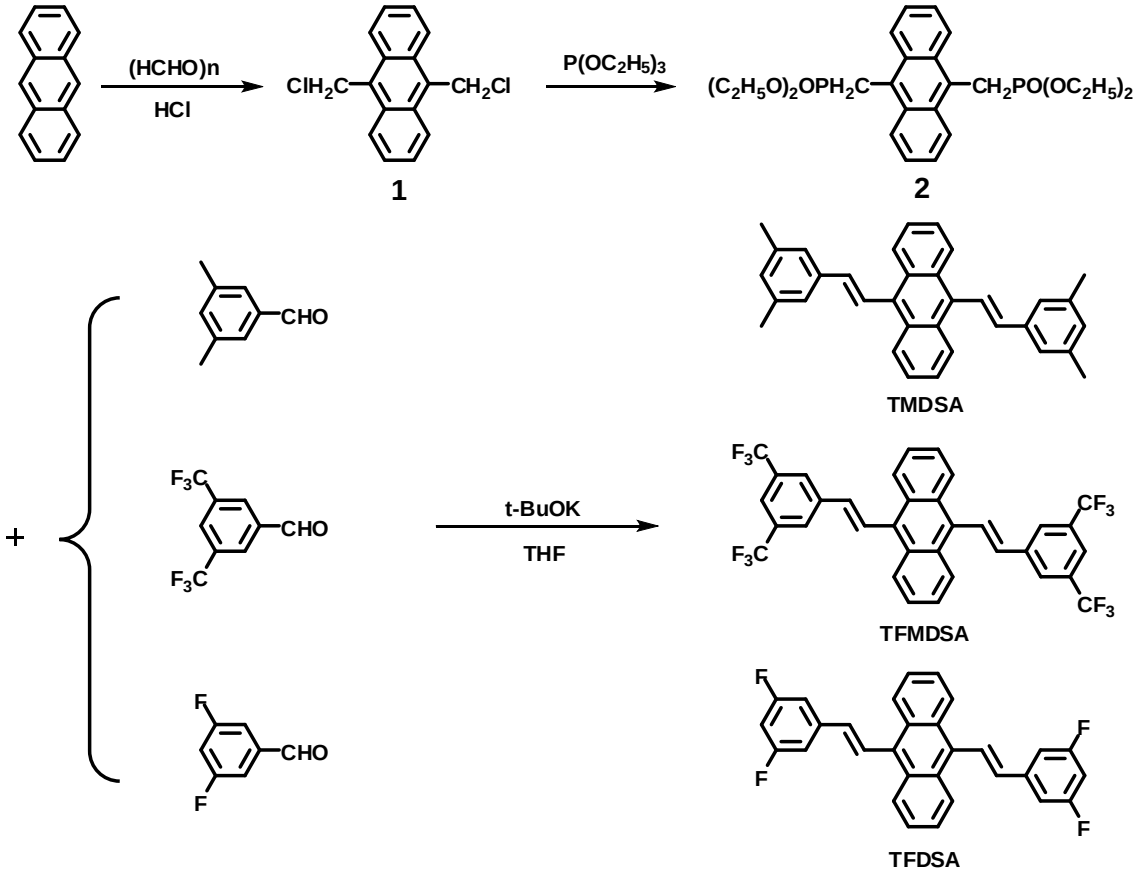


Scheme S1. Synthesis route of TMDSA, TFMDSA and TFDSA

Synthesis

Synthesis of (1) 9,10-bis(dichloromethyl)anthracene.

A two-necked bottle (500 mL) was oven-dried, anthracene (18 g，0.1 mol) was dissolved in 1,4-dioxane (144 ml) and HCl (24 mL). Paraformaldehyde (15.2 g) was added to the solution and the mixture was stirred for 2 h at 110 °C under HCl atmosphere. After removing the HCl atmosphere, the reaction went on stiring for 4 h at this temperature. The reaction mixture was cooled to room temperature and washed by 1,4-dioxane and neutralized by water to give compound as yellow powder 12.3 g (40% yield). ^{1}H NMR(500 MHz $CDCl_3$) δ 8.366-8.346 (m, 4H, Ar), 7.638-7.618 (m, 4H, Ar), 5.580 (s, 4H, CH_2).

Synthesis of (2) tetraethyl anthracene-9,10-diylbis(methylene)diphosphonate

Compound (1) (17 g, 50 mmol) was dissolved in $P(OC_2H_5)_3$ (86.5 ml, 0.5 mol). The reaction mixture was heated to 150 °C in an oil bath and stirred for 18 h at this temperature under N_2 atmosphere. After being cooled to room temperature, the reaction mixture was poured into petroleum ether and filtered to give 18 g of compound (2) as a light yellow solid (75% yield). ^{1}H NMR(500 MHz $CDCl_3$) δ

8.388-8.354 (m, 4H, Ar), 7.582-7.548 (m, 4H, Ar), 4.263-4.196 (d, 4H, CH_2), 3.931-3.777 (m , 8H, CH_2), 1.080-1.033 (t, 12H, CH_3).

Synthesis of 9,10-bis(3,5-dimethylstyryl)anthracene (TMDSA).

Compound tetraethylanthracene-9,10-diylbis(methylene)diphosphonate (0.600 g, 1.25 mmol) was stirred with Bu^tOK (0.421 g, 3.76 mmol) in THF (200 mL) under nitrogen. Compound 3,5-dimethylbenzaldehyde (0.38 mL, 2.84 mmol) in THF (50 mL) was added to the solution that was kept in an ice-bath and the mixture was stirred for 12 h at room temperature. The resultant precipitate was washed successively with MeOH and filtered off to give compound as yellow powder (75% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41-8.39 (m, 4H), 7.91 (d, *J* = 16.5 Hz, 2H), 7.48-7.46 (m, 4H), 7.02 (s, 2H), 7.02 (s, 2H), 6.89 (d, *J* = 16.5 Hz, 2H), 2.42 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 138.39 (s, Ar), 137.66 (s, Ar), 137.26 (s, Ar), 132.82 (s, Ar), 129.79 (s, Ar), 129.61 (s, Ar), 126.53 (s, CH=CH), 125.18 (s, CH=CH), 124.79 (s, Ar), 124.50 (s, Ar), 21.39 (s, CH_3). MALDI/TOF MS calcd for $C_{34}H_{30}$ 438.2, found 438.6. Anal. Calcd for $C_{34}H_{30}$: C, 93.11; H, 6.89. Found: C, 93.13; H, 6.87.

Synthesis of 9,10-bis(3,5-bis(trifluoromethyl)styryl)anthracene (TFMDSA).

TFMDSA was prepared according to the same procedure as that of **TMDSA** to give compound as yellow powder (55% yield). ^{1}H NMR (500 MHz, CDCl3): δ 8.35-8.33 (m, 4H), 8.12 (d, J = 16.5 Hz, 2H), 8.10 (s, 4H), 7.87 (s, 2H), 7.55-7.53 (m, 4H), 7.03 (d, *J* = 16.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 139.12 (s, Ar), 134.81 (s, Ar), 132.47-131.90 (m, CF_3), 129.44 (s, Ar), 129.24 (s, Ar), 126.37 (s, CH=CH), 126.35 (s, CH=CH), 126.12 (s, Ar), 125.91 (s, Ar), 121.43 (s, Ar), 29.71 (s, Ar). MALDI/TOF MS calcd for $C_{34}H_{18}F_{12}$ 654.1, found 653.8. Calcd for $C_{34}H_{18}F_{12}$: C, 62.39; H, 2.77; F, 34.83. Found: C, 62.35; H, 2.80; F, 34.84.

Synthesis of 9,10-bis(3,5-difluorostyryl)anthracene (TFDSA).

TFDSA was prepared according to the same procedure as that of **TMDSA** to give compound as yellow powder (65% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33-8.30 (m, 4H), 7.94 (d, *J* = 16.5 Hz, 2H), 7.52-7.48 (m, 4H), 7.18 (d, 4H), 6.85 (d, *J* = 16.5 Hz, 2H), 6.81 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 164.50-162.43 (dd, C-F), 140.51 (t, Ar), 135.53 (s, Ar), 132.02 (s, Ar), 129.45 (s, Ar), 127.86 (s, Ar), 126.20 (s, CH=CH), 125.68 (s, CH=CH), 109.27 (d, Ar), 103.25 (t, Ar). MALDI/TOF MS calcd for $C_{30}H_{18}F_4$ 454.1, found 454.5. Anal. Calcd for $C_{30}H_{18}F_4$: C, 79.29; H, 3.99; F, 16.72. Found: C, 79.28; H, 4.01; F, 16.71.

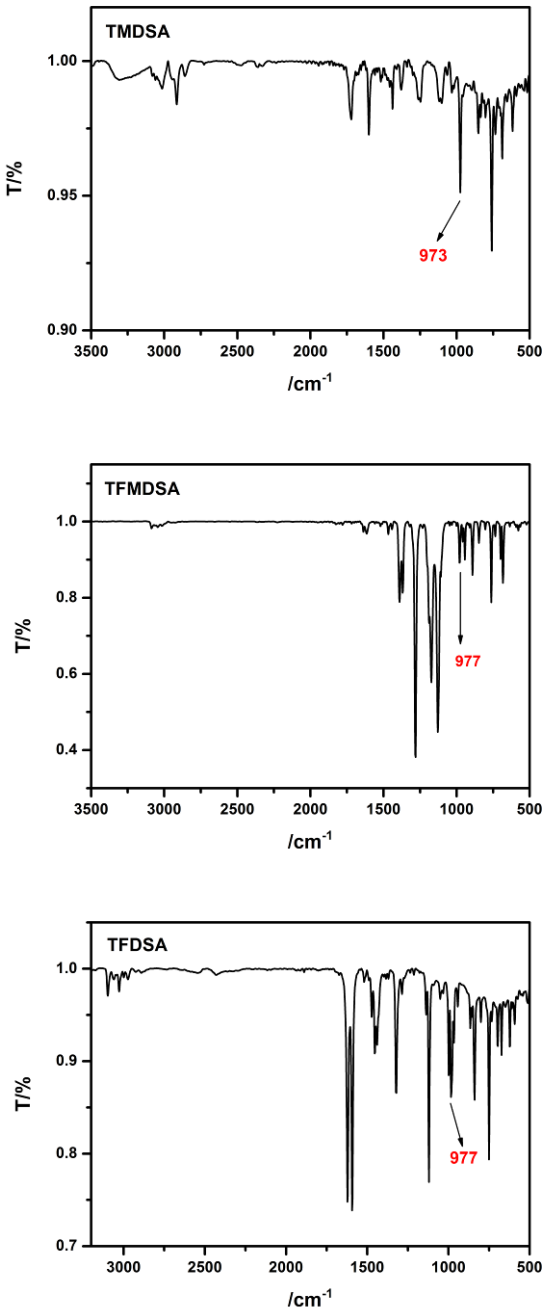


Figure S1. FT-IR absorption spectra (KBr pellets) of TMDSA, TFMDSA and TFDSA. The arrows show the stretching peaks of the *trans*-double bond.

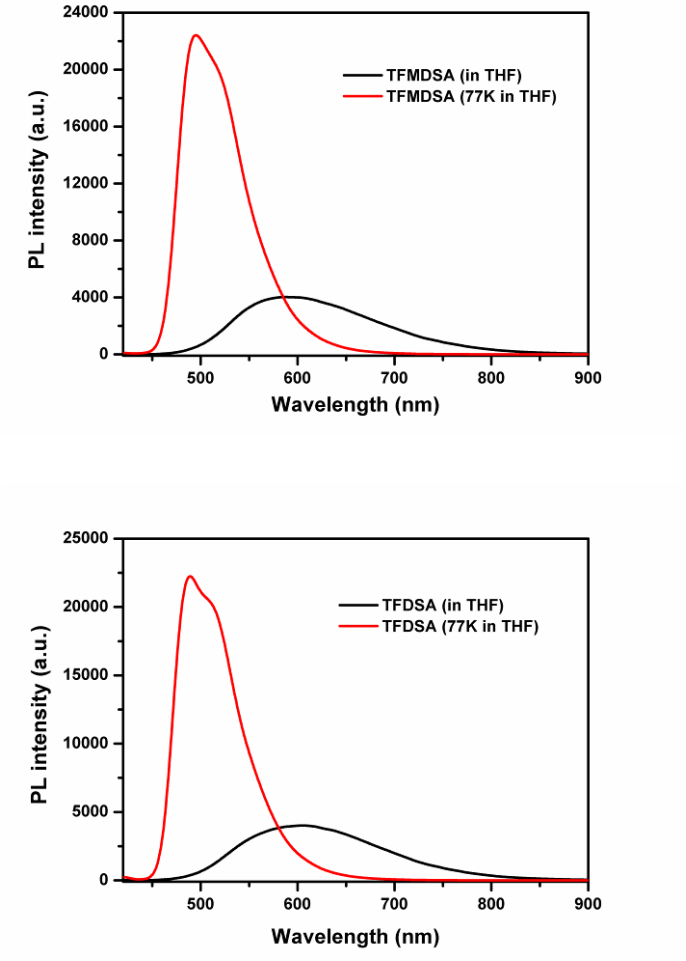
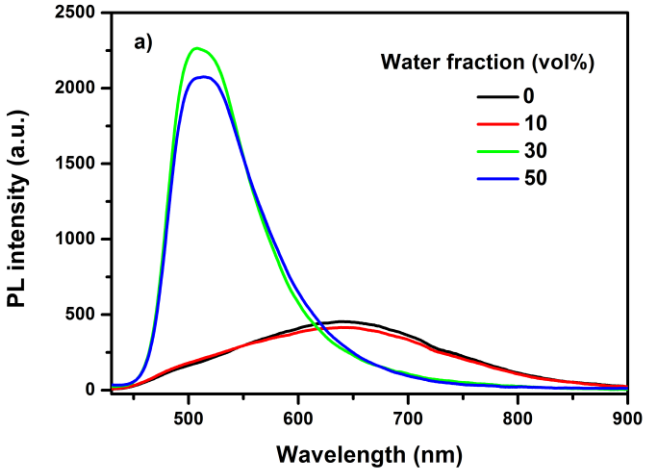


Figure S2. PL spectra of TFMDSA and TFDSA in THF solution at room temperature and 77 K at concentration of ~10^{-5} M.



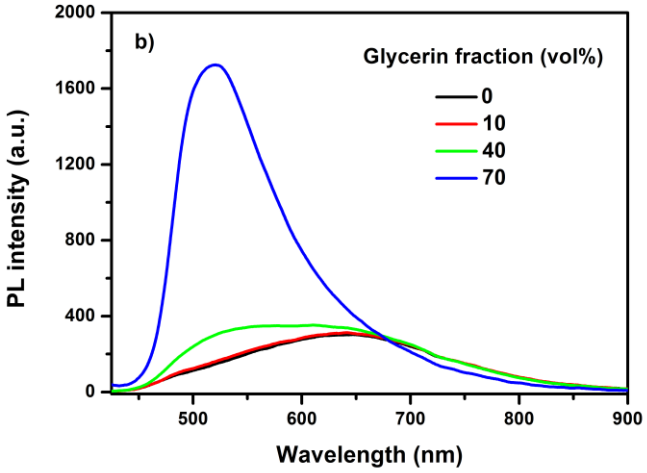


Figure S3. PL spectra of TMDSA in DMF-Water (a) and DMF-Glycerin (b) mixtures at concentration of ~10^{-5} M.

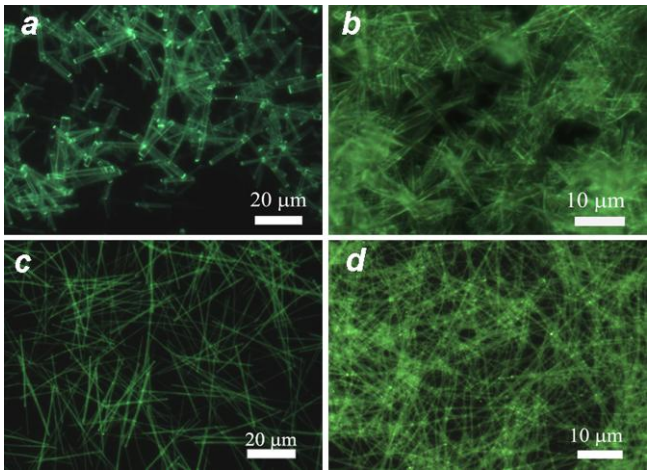


Figure S4. Fluorescence images of DSA (a), TMDSA (b), TFMDSA (c) and TFDSA (d) prepared by reprecipitation process.

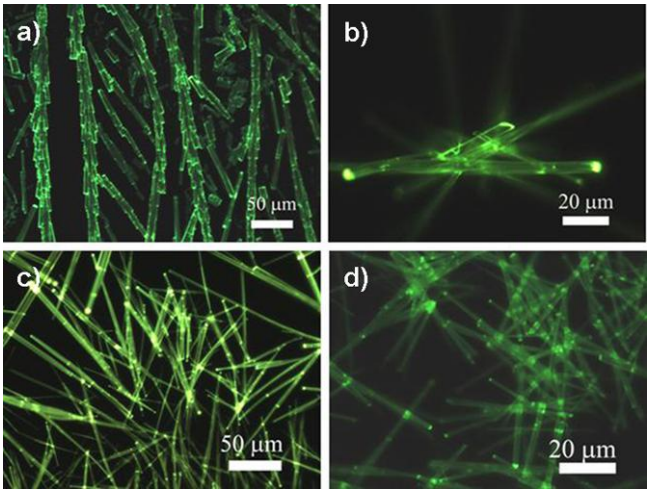


Figure S5. Fluorescence images of DSA (a), TMDSA (b), TFDSA (c) and TFMDSA (d) prepared by evaporation.

Table S1: Crystal Data and Structure Refinements of Three Crystals

	TMDSA	TFDSA	TFMDSA
empirical formula	$C_{34}H_{30}$	$C_{30}H_{18}F_4$	$C_{34}H_{18}F_{12}$
formula wt	438.58	454.44	654.48
T, K	293(2)	293(2)	293(2)
crystal system	monoclinic	triclinic	monoclinic
space group	P2(1)/c	P-1	P2(1)/c
a, Å	7.7071(15)	4.0152(8)	4.8750(10)
b, Å	30.672(6)	9.821(2)	13.857(3)
c, Å	5.2356(10)	13.736(3)	20.296(4)
α,deg	90.00	78.74(3)	90.00
β,deg	94.83(3)	86.02(3)	92.85(3)
γ,deg	90.00	84.26(3)	90.00
V,Å^3	1233.3(4)	527.88(18)	1369.4(5)
Z	2	1	2
density, mg/m^3	1.181	1.430	1.587
μ (Mo K α), *mm*$^{-1}$	0.066	0.107	0.149
θ range, deg	2.97-24.99	3.03-27.55	3.11-24.99
no.of reflcns collected	9431	4984	9672
no. of unique reflcns	2172	2276	2377
R(int)	0.0665	0.0468	0.2914
GOF	1.010	1.077	0.934
R_1 [$I > 2\sigma(I)$]	0.0766	0.0610	0.0905
wR_2 [$I > 2\sigma(I)$]	0.2154	0.1623	0.1588
R_1 (all data)	0.1178	0.1147	0.3116
wR_2 (all data)	0.2451	0.1885	0.2568