Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Realizing highly efficient blue photoluminescence of dimethylsilane-aryl (phenylene, diphenylene, fluorenyl) main-chain polymers with σ-π conjugation

*Wenyan Huang[1], Yeqi Zhu[1], Lei Zhong[1], Chao Jin[1], Yinong Zheng[1], Yinggan Zhang[1], Siqi Lan[1], Shiwen Gong[1], Jiangnan Zhao[1], Meng Huang[1], Rongqian Yao[1]**

[1]College of Materials, Fujian Key Laboratory of Advanced Materials (Xiamen University), and Key Laboratory of High Performance Ceramics Fibers (Xiamen University), Ministry of Education, China, Xiamen, Fujian 361005, P. R. China

Corresponding Author

*E-mail: rqyao@xmu.edu.cn (R. Yao).

Contents

1 Chemical structure

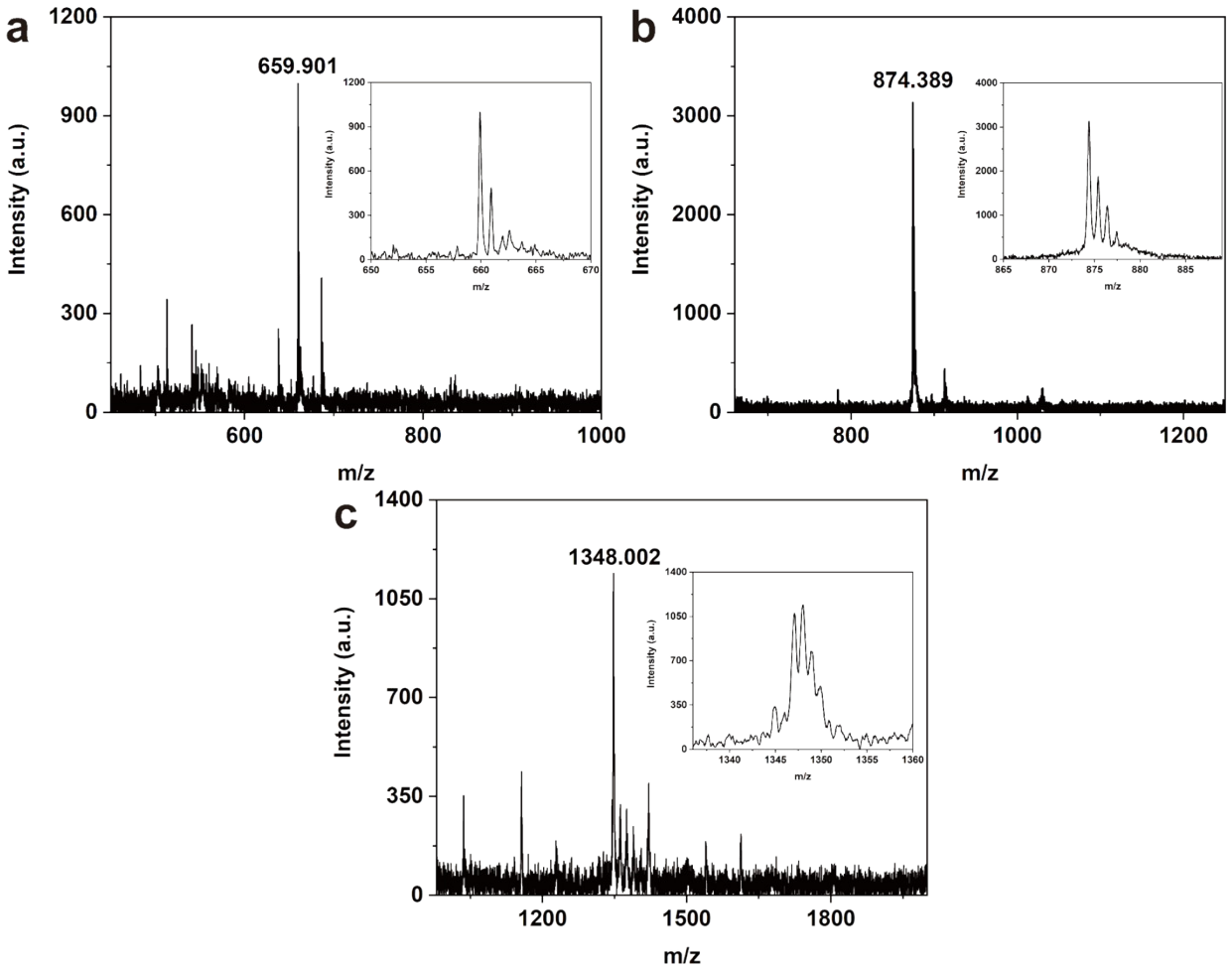

Figure S1. MALDI-TOF MS spectra of (a) PPCS, (b) PDCS and (c) PFCS.

Table S1. Detailed features of products obtained by MALDI-TOF MS.

Sample	m/z [Da]	m[a)]	n[a)]	Chemical formula[a)]
PPCS	659.901 $[M + K]^+$	8	2	$Si_8C_{28}H_{58}$
PDCS	874.389 $[M + Na]^+$	12	1	$Si_{12}C_{36}H_{82}$
PFCS	1348.002 $[M + K]^+$	14	3	$Si_{14}C_{67}H_{110}$

[a)] Estimated from MALDI-TOF MS spectra as depicted in Figure S1.

2 Photophysical properties

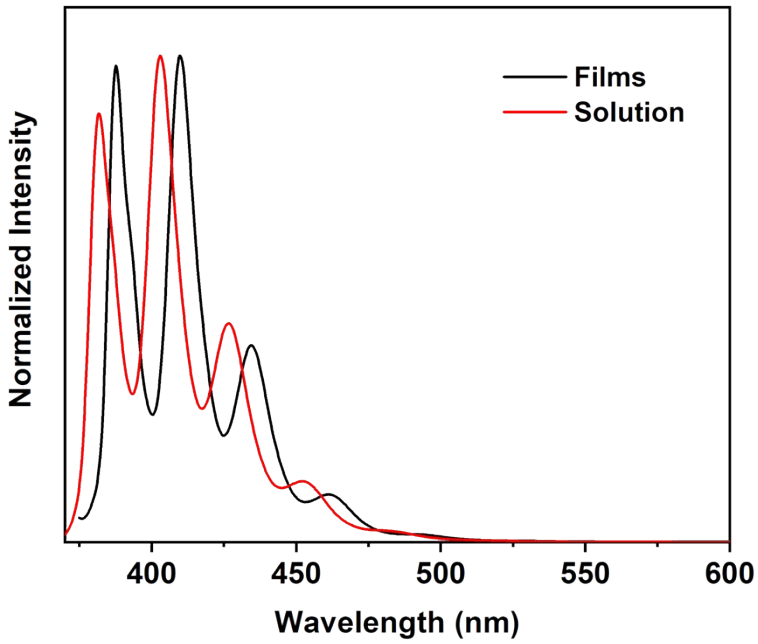

Figure S2. PL spectra of reference monomer (fluorene) films and solution.

Fluorene monomer solution was made by THF (10^{-6}-10^{-5} mol·L^{-1}) and its monomer films were prepared by spin-coating with THF as solvent (15-20 mg·mL^{-1}) at 2100 rpm for 30 s. Their emission characterization was performed and the results were shown in Figure S2. PL spectrum of fluorene in solution state exhibits multiple peaks at about 382 nm, 403 nm, 427 nm and 452 nm. For fluorene in film state, multiple peaks at about 388 nm, 410 nm, 434 nm and 461 nm generate bathochromic shift owing to the aggregation among monomer molecules. The S_1-S_0 energy gap ($\Delta E_{S1\rightarrow S0}$)[3] of fluorene monomer and PFCS films are calculated to be 3.20 eV and 3.02 eV respectively. In addition, absolute photoluminescence quantum yield (PLQY) of phenyl, diphenyl and fluorene core groups with intermolecular interactions is about 5%, 23% and 72%, respectively[4-6]. Indeed, PFCS products possess improved photophysical properties including red-shifted peaks, low energy gap, extended conjugation and enhanced blue emission in comparison with fluorene monomer, which are beneficial to practical applications.

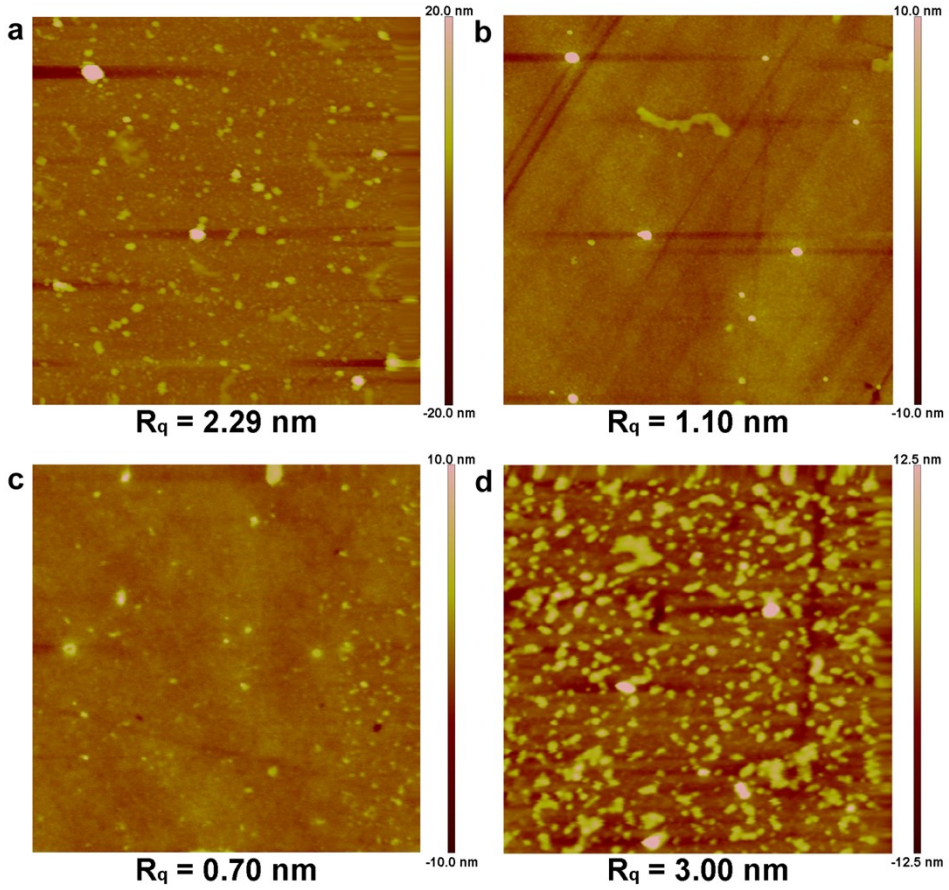

Figure S3. AFM height images (2 μm × 2 μm) of (a) PPCS, (b) PDCS, (c) PFCS and (d) monomer fluorene spin-coated onto quartz glasses.

Table S2. Fluorescence lifetime data of PPCS, PDCS and PFCS.

Sample	τ_1/ns [Rel%, η_1]	τ_2/ns [Rel%, η_2]	τ/ns
PPCS films	0.37 (51.09%)	1.99 (48.91%)	1.16
PDCS films	0.38 (63.20%)	1.85 (36.80%)	0.92
PFCS films	0.27 (61.45%)	1.57 (38.55%)	0.77
PPCS solution	1.97	–	1.97
PDCS solution	3.04	–	3.04
PFCS solution	0.73	–	0.73

To gain an idea about the rate of relaxation in the excited state, the radiative (k_r) and non-radiative (k_{nr}) rate constants have been calculated using following two equations[1,2]:

$$k_r = \frac{\Phi_{PL}}{\tau} \#(1)$$

$$k_{nr} = \frac{1 - \Phi_{PL}}{\tau} \#(2)$$

where Φ_{PL} is the emission yield and τ is the fluorescence lifetime value for the polymer.

Table S3. Photophysical properties of PPCS, PDCS and PFCS.

Sample	Φ_{PL}	τ_f[a)] [ns]	k_{rf}[b)] [s^{-1}]	k_{nrf}[c)] [s^{-1}]	τ_s[d)] [ns]	k_{rs}[e)] [s^{-1}]	k_{nrs}[f)] [s^{-1}]
PPCS	64.26%	1.97	3.262×10^8	1.814×10^8	1.16	5.540×10^8	3.081×10^8
PDCS	66.63%	3.04	2.192×10^8	1.098×10^8	0.92	7.242×10^8	3.627×10^8
PFCS	89.75%	0.73	1.229×10^9	1.404×10^8	0.77	1.166×10^9	1.331×10^8

[a)] Fluorescence decay lifetime of films (τ_f); [b)] The radiative rate constants of films (k_{rf}); [c)] The non-radiative rate constants of films (k_{nrf}); [d)] Fluorescence decay lifetime of solutions (τ_s); [e)] The radiative rate constants of solutions (k_{rs}); [f)] The non-radiative rate constants of solutions (k_{nrs}).

3 Electrochemical properties

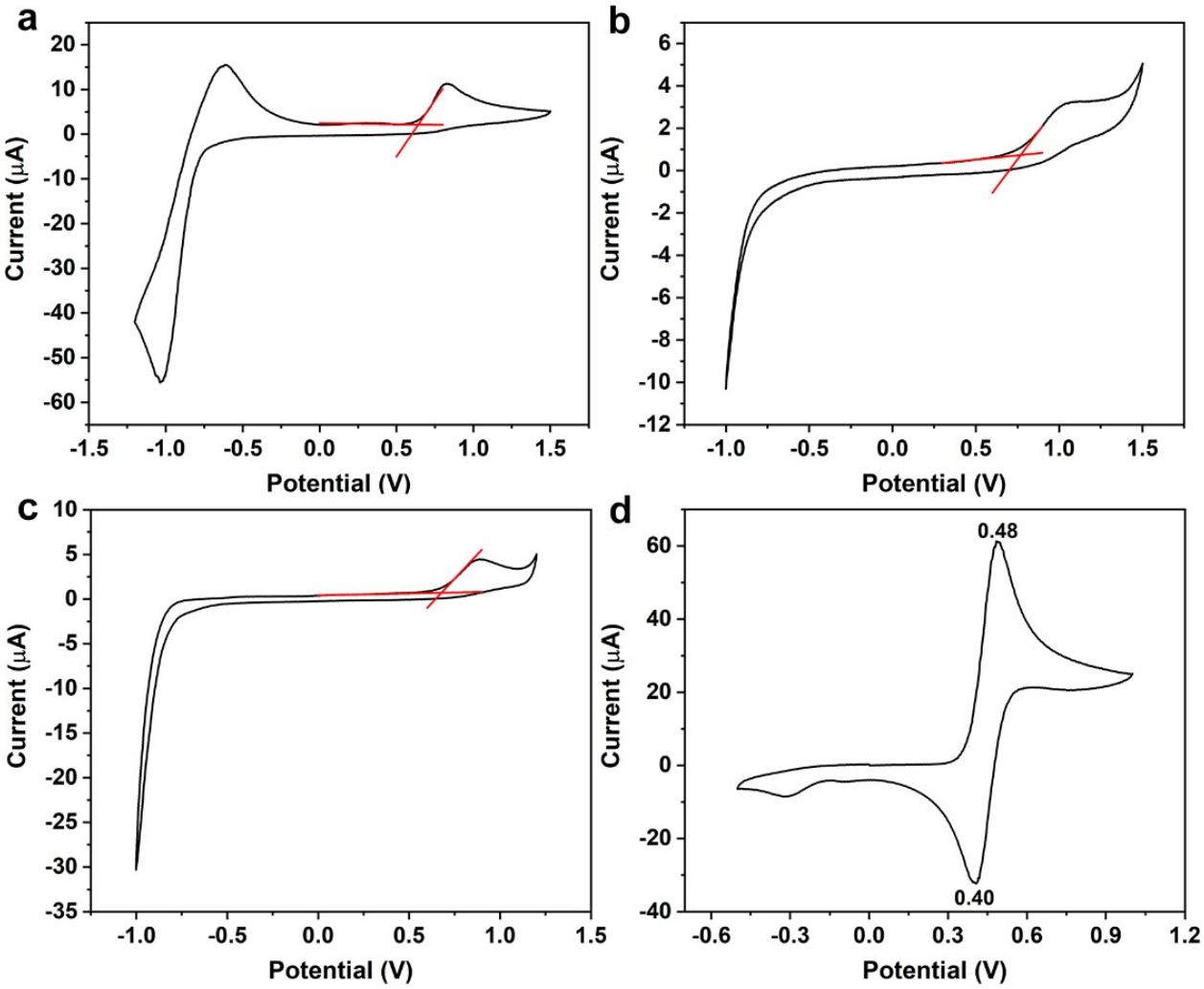

Figure S4. Cyclic voltammograms for the oxidation of (a) PPCS, (b) PDCS and (c) PFCS; (d) Redox potential of ferrocene (0.1 mmol) in tetrabutylammonium hexafluorophosphate (0.1 mol·L^{-1}) acetonitrile solution.

References

1 J. V. Caspar and T. J. Meyer, *J. Phys. Chem.*, 1983, **87**, 952–957.

2 J. K. Rice, E. D. Niemeyer and F. V Bright, *J. Phys. Chem.*, 1996, **100**, 8499–8507.

3 X. Wang, H. Shi, H. Ma, W. Ye, L. Song, J. Zan, X. Yao, X. Ou, G. Yang, Z. Zhao, M. Singh, C. Lin, H. Wang, W. Jia, Q. Wang, J. Zhi, C. Dong, X. Jiang, Y. Tang, X. Xie, Y. Yang, J. Wang, Q. Chen, Y. Wang, H. Yang, G. Zhang, Z. An, X. Liu and W. Huang, *Nat. Photonics*, 2021, **15**, 187–192.

4 D. Liu, J. De, H. Gao, S. Ma, Q. Ou, S. Li, Z. Qin, H. Dong, Q. Liao, B. Xu, Q. Peng, Z. Shuai, W. Tian, H. Fu, X. Zhang, Y. Zhen and W. Hu, *J. Am. Chem. Soc.*, 2020, **142**, 6332–6339.

5 S. Kim, B. Kim, J. Lee, H. Shin, Y.-I. Park and J. Park, *Mat. Sci. Eng. R*, 2016, **99**, 1–22.

6 A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213–2228.