Enhanced stability of rubrene analogue with lamellar packing motif

Jinfeng Li,[a] Zhenjie Ni,[b] Xiaotao Zhang,*[a] Rongjin Li,[a] Huanli Dong[b] and Wenping Hu*[a]

a. Tianjin Key Laboratory of Molecular Optoelectronic Sciences,

Department of Chemistry, School of Science, Tianjin University & Collaborative Innovation Centre of Chemical Science and Engineering (Tianjin), Tianjin 300072,

b. Beijing National Laboratory for Molecular Science, Key Laboratory of Organic Solids, Institute of Chemistry,Chinese Academy of Sciences, Beijing 100190, China

***Correspondence: zhangxt@tju.edu.cn; huwp@tju.edu.cn**

Table of contents

Experimental Section

Materials and Instrumentations

Toluene (HPLC), dry CH_2Cl_2 and dry THF can get from commercial sources. Other materials and solvents are commercially available and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvent on a Bruker DMX-400 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. UV-vis measurements were performed using a JASCO V-570 UV-vis spectrometer. Cyclic voltammograms were recorded with a CHI660C electrochemistry station. The working electrode was glassy carbon, the counter and reference electrodes was Pt wire and Ag/AgCl respectively. Voltammograms were recorded in deaerated (argon bubbling) dry CH_2Cl_2 using tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte. X-Ray diffraction (XRD) measurements were obtained from a 2 kW Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation. The reflection mode for voltage and current were 40 kV and 200 mA respectively. Computational details were performed by using density functional theory (DFT) calculations through Gaussian 09 Revision at the B3LYP/6-311G (d,p) level.

Synthesis of Compound **2** and Compound **SF_{10}-RUB**

Compound **2**: To a solution of 2-ethynylthiophene (21.95 mmol, 1.0 equiv.) in dry THF (80 mL), n-BuLi (2.4 M in hexanes, 10.1 mL, 1.1 equiv.) was added at -78 ^{o}C under nitrogen atmosphere. The solution allowed to stir for 40 min at -78 ^{o}C before a solution of (perfluorophenyl)(phenyl)methanone (21.95 mmol, 1 equiv.) in dry THF (20 mL) were added slowly. After the mixture stirred for another 15 min, the resulting solution was slowly warmed up to room temperature and stirred for 10 h. Saturated aqueous NH_4Cl (40 mL) was added to the solution and extracted with CH_2Cl_2 (3 x 40 mL). Then combined organic layer were washed with brine (40 mL), dried with $MgSO_4$, concentrated under reduced pressure. Purified by flash column chromatography on silica gel (eluent: n-hexane–CH_2Cl_2=1:3) to give brown solids of compound 2

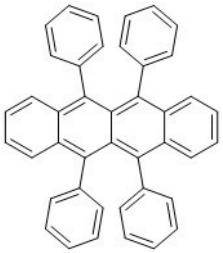
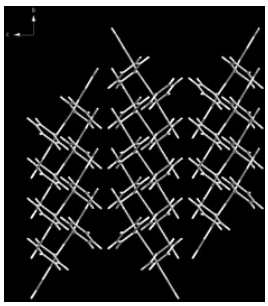
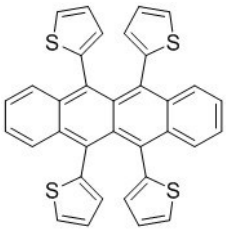
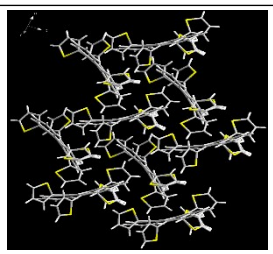
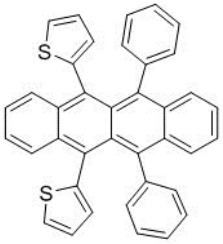
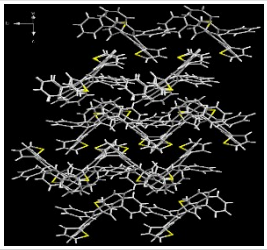
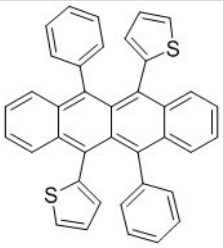
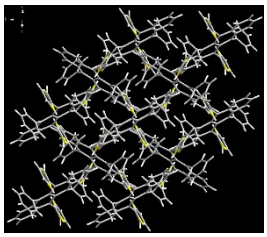
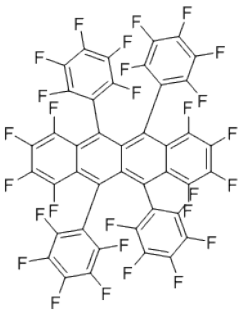
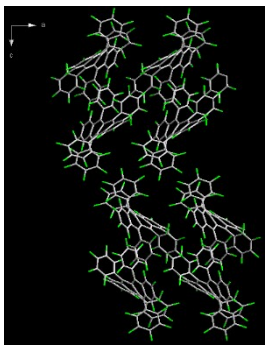
(11 mmol, yield: 75%). ^{1}HNMR (400MHz, $CDCl_3$) d (ppm): 7.73 (d, 2H), 7.44 (t, 2H), 7.40 (d, 1H), 7.38 (d, 1H), 7.05 (t, 1H), 7.34 (d, 1H), 3.57 (s, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) d (ppm): 142.97, 133.54, 129.18, 128.98, 128.79, 127.61, 126.00, 121.77, 92.37, 81.63, 72.77. HR-MS (EI) for $C_{19}H_9F_5OS$: calculated: 380.0294; Found: 380.0274.

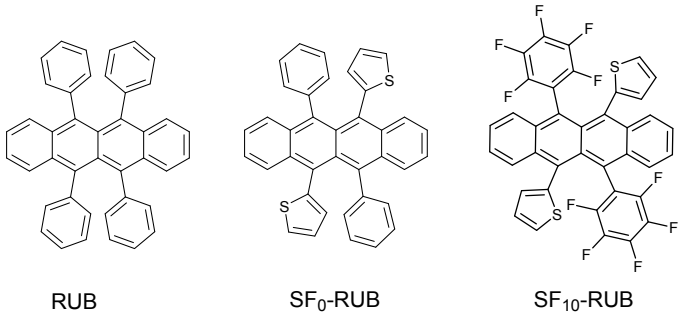
Compound **SF_{10}-RUB**: Propargyl alcohol 2, (2.8 g, 7.36mmole, 1equiv) was dissolved in dry toluene (30 mL), which was slight heated to get complete dissolution, then the mixture was cooled and stirred at 0 ^{o}C under a nitrogen atmosphere. Triethylamine (NEt_3) (1.43 mL, 10.3 mmole, 1.4 equiv) was added to this solution, then 4-toluene sulfonyl chloride ($C_7H_7ClO_2S$), (1.65 g, 8.61 mmole, 1.17 equiv) was added slowly. After the addition, the solution was stirred at 0 ^{o}C for 15 minutes, then the mixture was warmed to room temperature and stirred for another 15 minutes before heated to 110 ^{o}C for 4 hours. After this period, the reaction was cooled, diluted with ethyl acetate (100 mL) and washed with 2M HCl. The organic layer was collected, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: n-hexane) to give red solids. ^{1}HNMR (600MHz, CD_2Cl_2) d (ppm): 7.59 (d, 2H), 7.46 (d, 2H), 7.34 (m, 4H), 7.21 (d, 2H), 7.03 (t, 2H), 6.97 (s, 2H). ^{13}C NMR (400 MHz, CD_2Cl_2) d (ppm): 140.88, 133.01, 131.37, 130.60, 130.43, 130.39, 130.23, 128.36, 128.25, 127.99, 127.26, 127.09, 125.39, 125.21, 124.74, 124.70, 122.15. HR-MS (MALDI-TOF) for $C_{38}H_{14}F_{10}S_2$: calculated: 724.0377; found: 724.0371.

Crystal growth of RUB SF_0-FUB and SF_{10}-RUB

High-purity crystal of RUB is obtained from a physical vapor transport technique. Compound SF_0-RUB is grown by using mixture solvents (hexane- ethyl acetate 9:1 v/v) through slow evaporation at room temperature. Compound SF_{10}-RUB is obtained by slow evaporating the mixture solvents (CH_2Cl_2-toluene 1:1 v/v) at room temperature.

Table S1. Chemical structure of rubrene and some analogues.

Chemical structure	Molecular packing	Ref
		1
		2
		3
		2
		4



RUB SF_0-RUB SF_{10}-RUB

Fig. S1. Compound RUB, SF_0-RUB and SF_{10}-RUB.

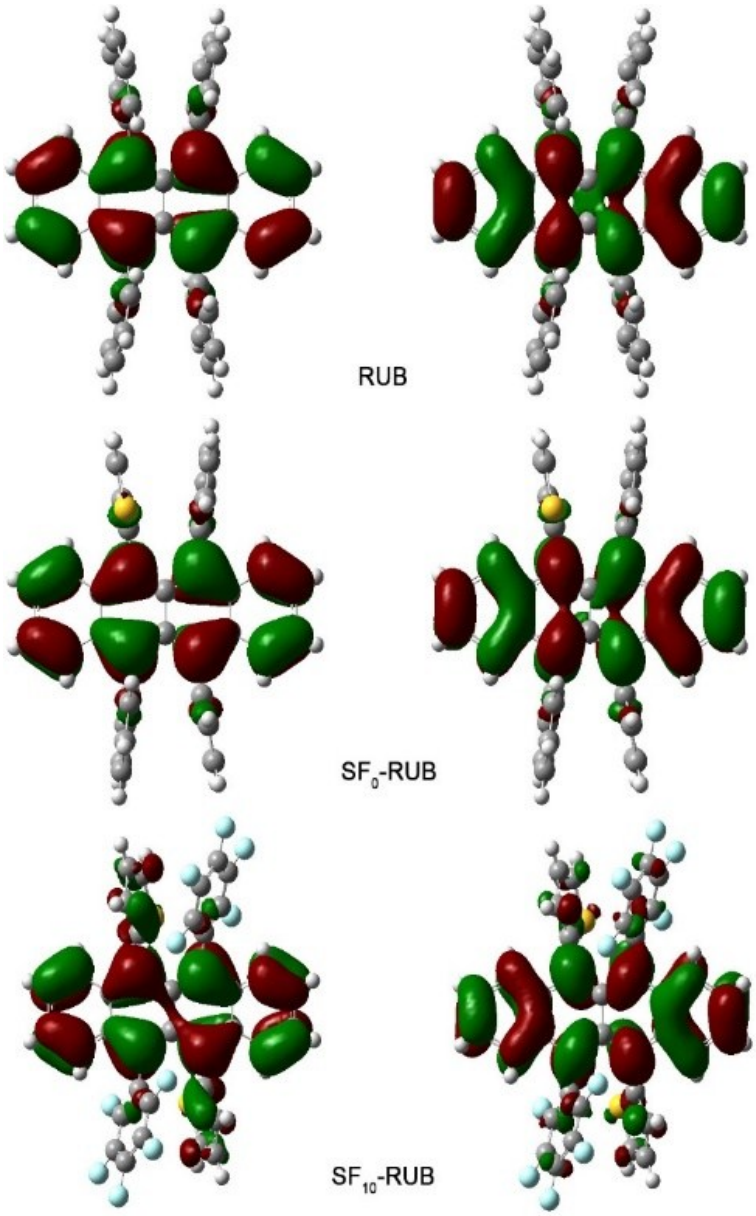


Fig. S2. HOMO (left) and LUMO (right) orbitals of **RUB**, **SF_0-RUB** and **SF_{10}-RUB** calculated by DFT theory.

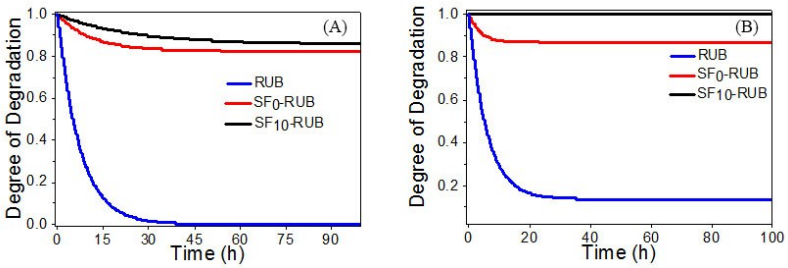


Fig. S3. Degree of degradation of SF_0-RUB and SF_{10}-RUB vs time ((A) in solution, (B) solid state).

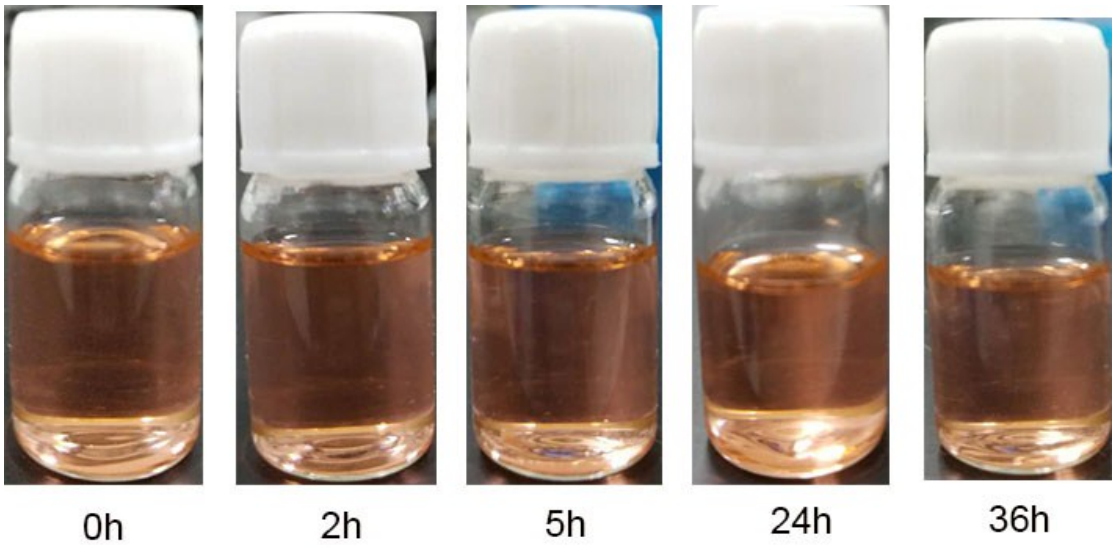


Fig. S4. SF_{10}-RUB in CH_2Cl_2 under normal atmosphere at different time.

Table S2. Single crystal diffraction data and structural refinement for **SF_{10}-RUB** (CCDC: 1026641)

Parameters	SF_{10}-RUB
Empirical formula	$C_{38}H_{14}F_{10}S_2$
Formula weight	724.61
Temperature	173(2) K
Wavelength	0.71073
Crystal system	orthorhombic
Space group	Pbcn
Unit cell dimensions	a=10.173(2) Å
	α = 90.00
	b=7.7560(16) Å
	β = 90.00
	c=27.693(6) Å
	γ = 90.00
Z	4
Density (calculated)	1.617 g cm^{-3}
Absorption coefficient	0.272
F(000)	1456
Crystal size (mm)	0.20 × 0.11 × 0.10
Theta range for	2.08° to 25.00°
data collection	
Index ranges	-16 ≤ *h* ≤ 16
	-5 ≤ *k*≤ 9
	-32 ≤ *l* ≤ 27
Reflections collected	14 172
Independent reflections	2615
R_{int}	0.0940
Completeness to theta	99.7%
Absorption correction	Multi-scan
Max. and min. transmission	1.00 and 0.5647
Data/restraints/parameters	3615/245/32
Goodness-of-fit on F^2	1.378
Final R indices	R_1 = 0.1122
[*I* > 2sigma(*I*)]	wR_2 = 0.1644
R indices (all data)	R_1 = 0.1336
	wR_2 = 0.1717
Largest diff. peak and hole	0.255 and -0.222 e $Å^{-3}$

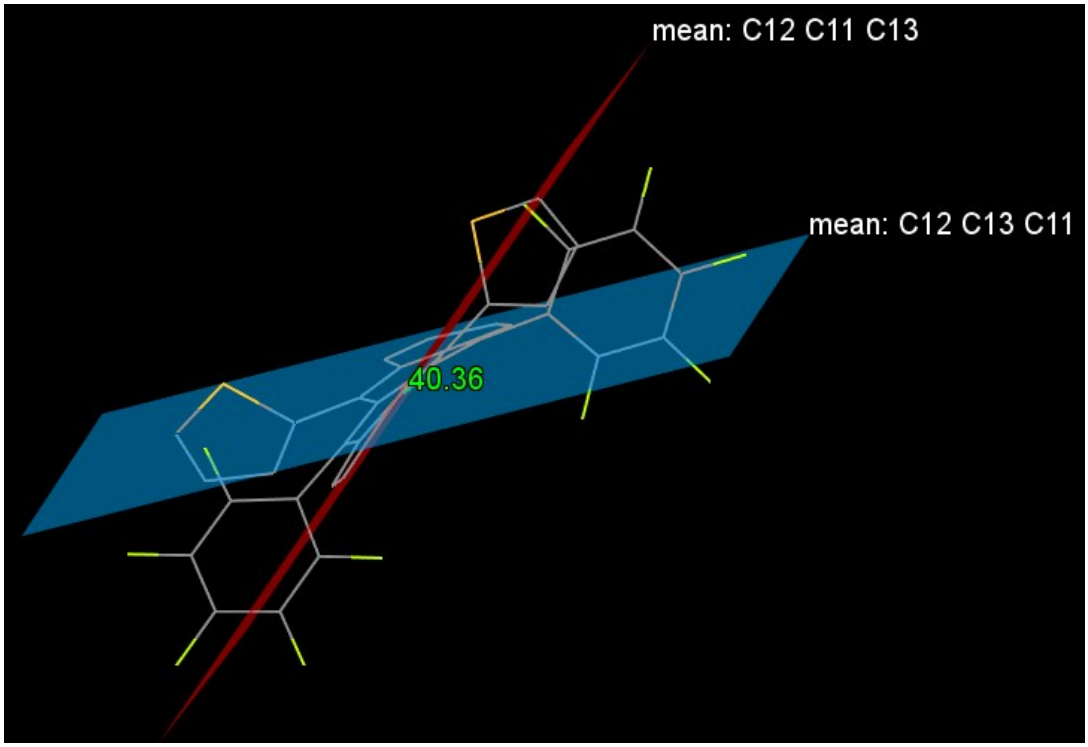


Fig. S4. Twist angle of SF_{10}-RUB

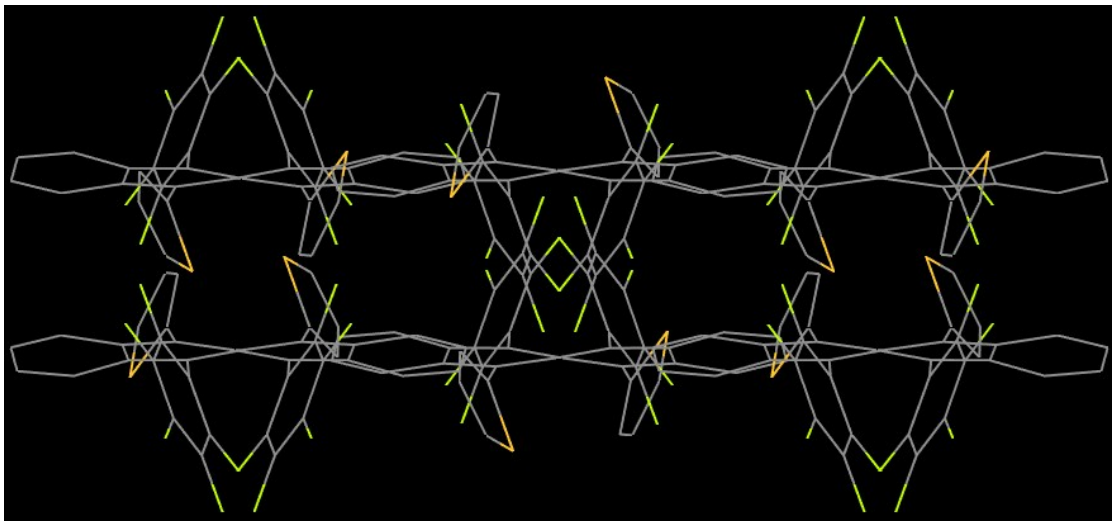


Fig. S5. Packing arrangements of SF_{10}-RUB (two thiophene rings is different with each other).

Reference:

1. S. Bergantin, M. Moret, G. Buth and F. P. A. Fabbiani, *The J. Phys. Chem. C*, 2014, **118**, 13476-13483.
2. X. Zhang, J. K. Sørensen, X. Fu, Y. Zhen, G. Zhao, L. Jiang, H. Dong, J. Liu, Z. Shuai, H. Geng, T. Bjørnholm and W. Hu, *J. Mater. Chem. C*, 2014, **2**, 884-890.
3. Y. Hou, X. Chi, X. Wan and Y. Chen, *J. Mol. Struct.*, 2008, **889**, 265-270.
4. Z. Zhang, W. A. Ogden, V. G. Young and C. J. Douglas, *Chem. Commun.*, 2016, **52**, 8127-8130.