Supporting Information

Synthesis of Optically Active Green Fluorescent π-Conjugated Fluorene Polymers Having Chiral Schiff Base in the Side Chain

K. Asai, G. Konishi,* K. Sumi, S. Kawauchi

konishi.g.aa@m.titech.ac.jp

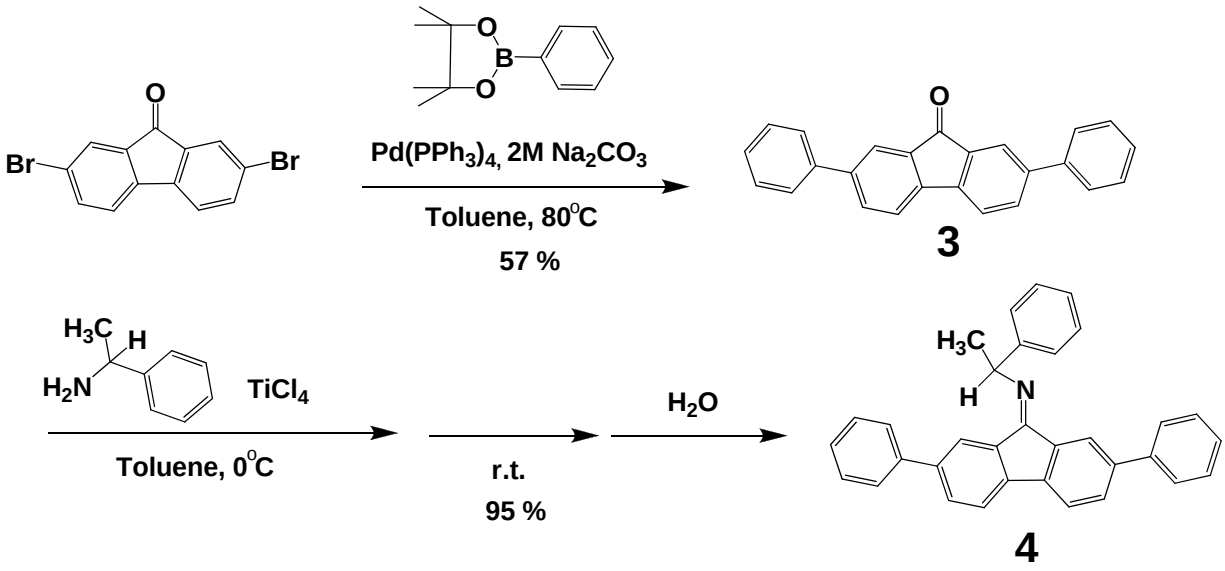
Experimental

2,7-diphenylfluorenone (3)

Synthesis of **3** was reported in 50's (Barnett, M. D.; Daub, G. H.; Hayes, F. Newton; O., Donald G., "Liquid scintillators. VI. 2-Aryl- and 2,7-diarylfluorenes." *J. Am. Chem. Soc*. **1959**, *81*, 4583.). Our procedure is as follows : To a solution of 2,7-dibromofluorenone (1.352 g, 4 mmol), (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1.837 g, 9 mmol), and $Pd(PPh_3)_4$ (1.0 mol %) in toluene (30 ml) was added 2M aqueous Na_2CO_3 solution under argon atmosphere. The mixture was degassed and stirred 90 °C. The mixture was extracted with toluene and the organic layer was washed with water and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (toluene : hexane = 1 : 1) as eluent to give 0.752g (57 %) of yellow solids. Further purification could be achieved by recrystallization from MeOH. ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.94 (d, 2H, *J* = 1.6 Hz), 7.75 (dd, 2H, *J* = 8.0, 1.6Hz), 7.65 (s, 2H), 7.63 (t, 4H, *J* = 8.0 Hz), 7.48 (t, 4H, *J* = 7.2 Hz), 7.39 (t, 2H, *J* = 7.2 Hz) ppm.; ^{13}C NMR (100 MHz, $CDCl_3$) : 193.7, 143.1, 142.2, 140.0, 135.2, 133.3, 129.0, 128.0, 126.8, 123.0, 120.7 ppm.; FT-IR (KBr) : 3057 (Ar–H), 1709 (C=O), 1604 (Ar–C–C) cm^{-1}.

See, **Figure S8, S12, S19.**

Scheme



Scheme S1.

Figures

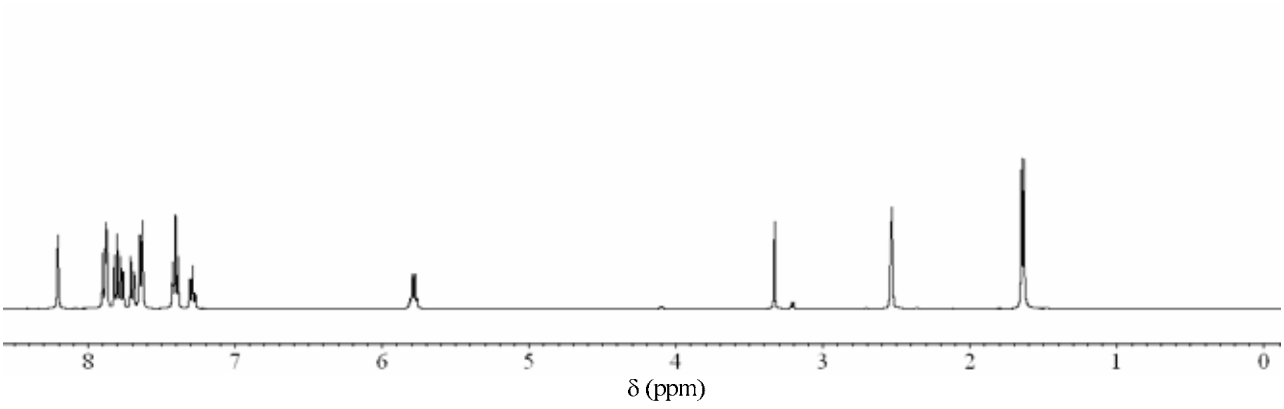


Figure S1. ^{1}H NMR spectrum of **1R** in DMSO-d_6 at 30 ^{o}C.

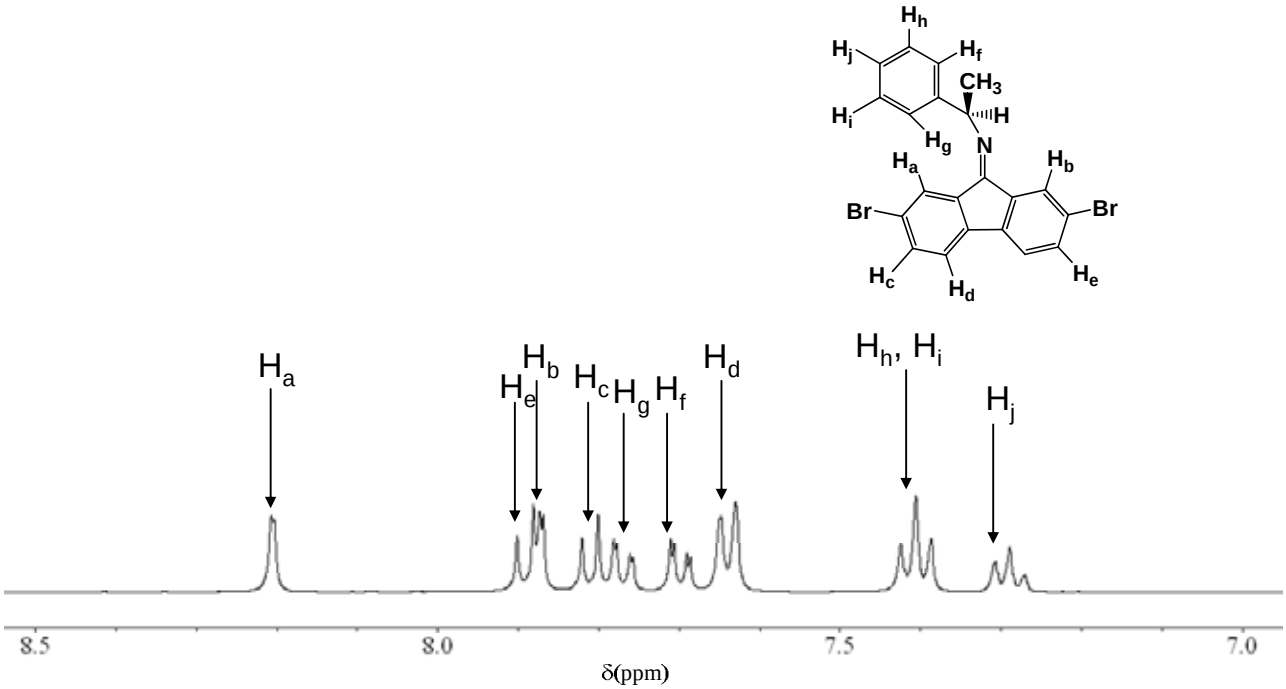


Figure S2. ^{1}H NMR spectrum of **1R** from 7.0-8.3 ppm in DMSO-d_6 at 30 ^{o}C.

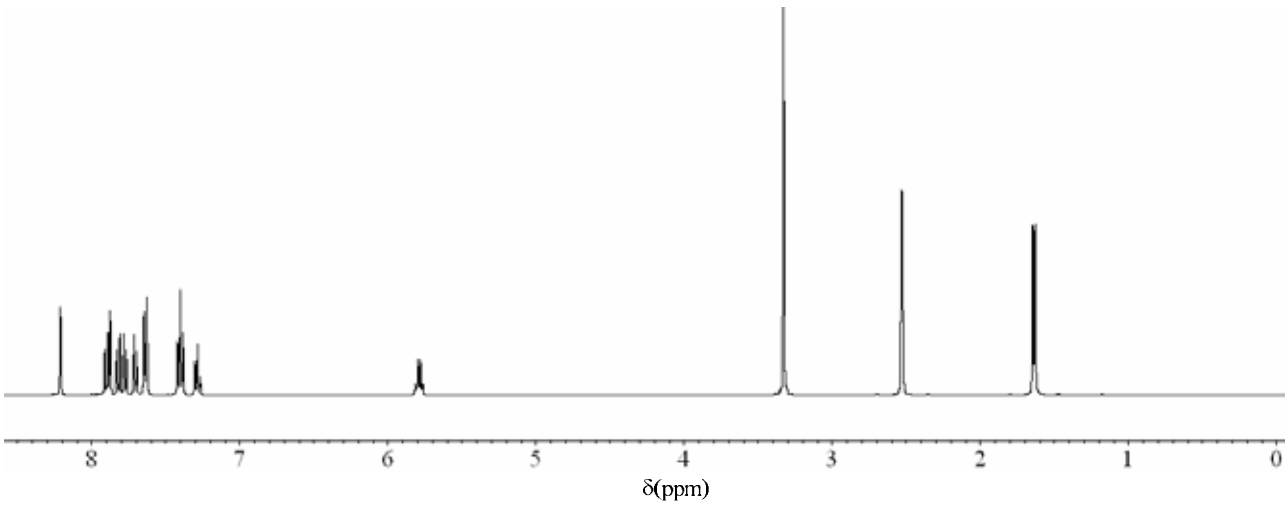


Figure S3. ^{1}H NMR spectrum of **1S** in DMSO-d_6 at 30 ^{o}C.

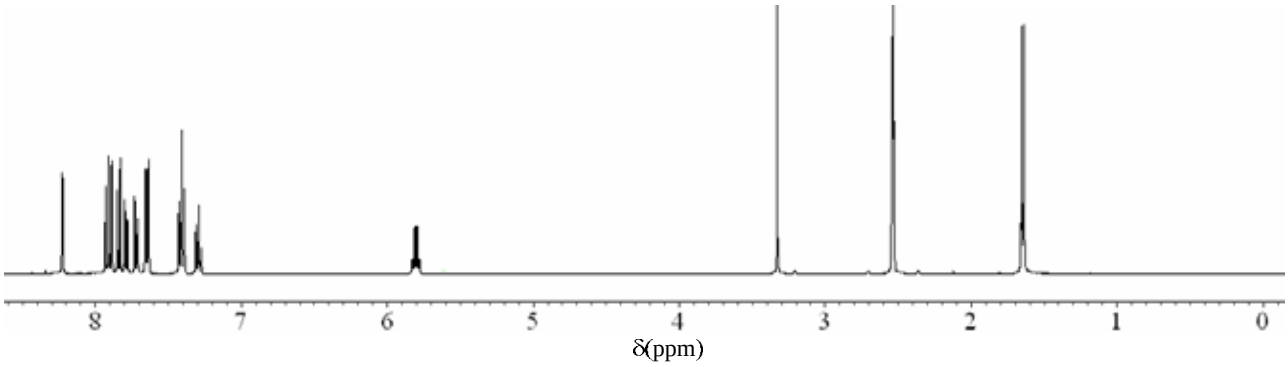


Figure S4. ^{1}H NMR spectrum of **1rac** in DMSO-d_6 at 30 ^{o}C.

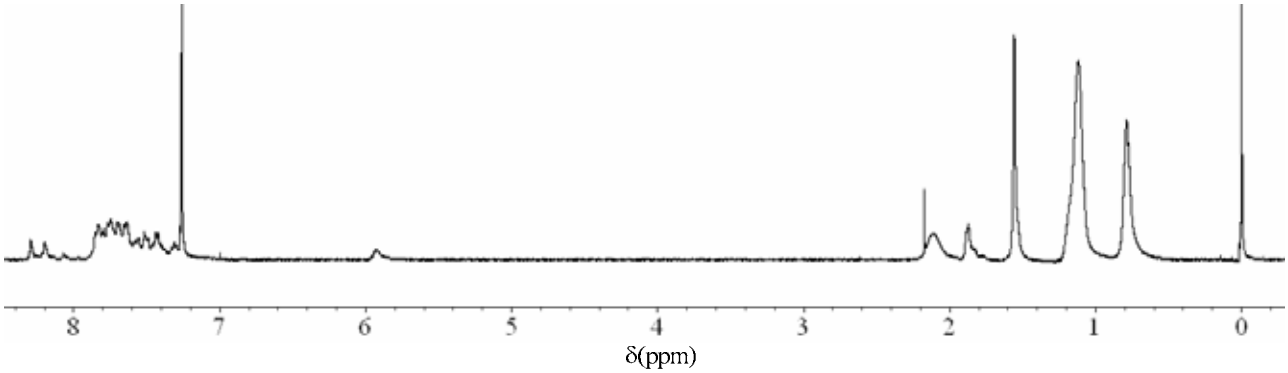


Figure S5. ^{1}H NMR spectrum of **2R** in $CDCl_3$.

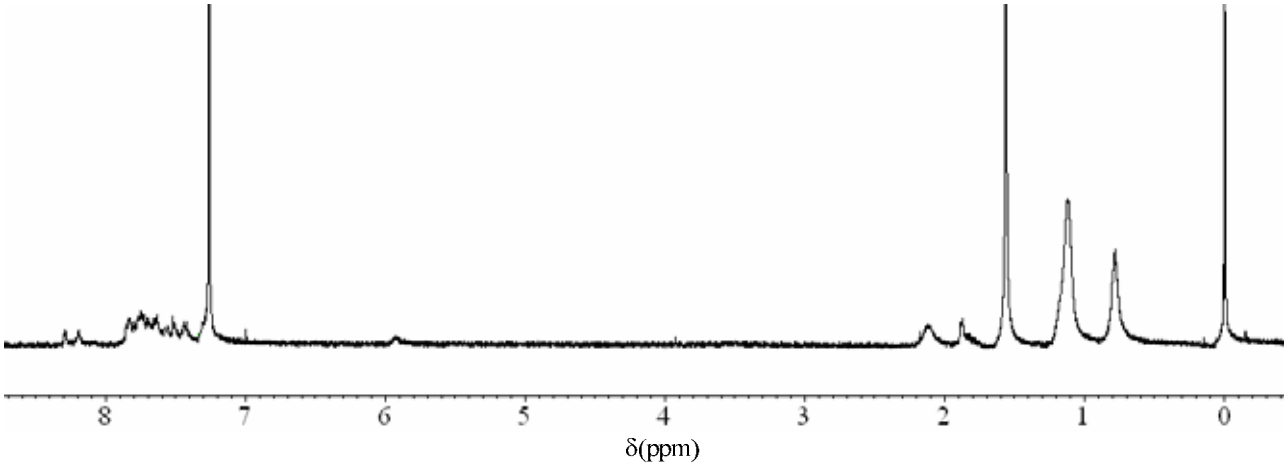


Figure S6. ^{1}H NMR spectrum of **2S** in $CDCl_3$.

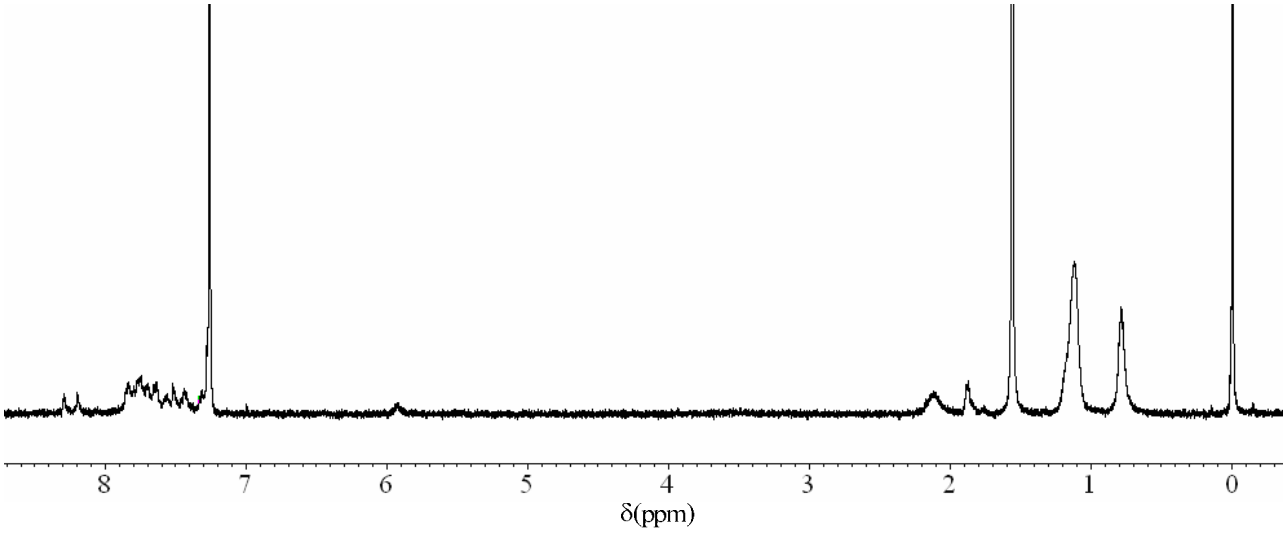


Figure S7. ^{1}H NMR spectrum of **2rac** in $CDCl_3$.

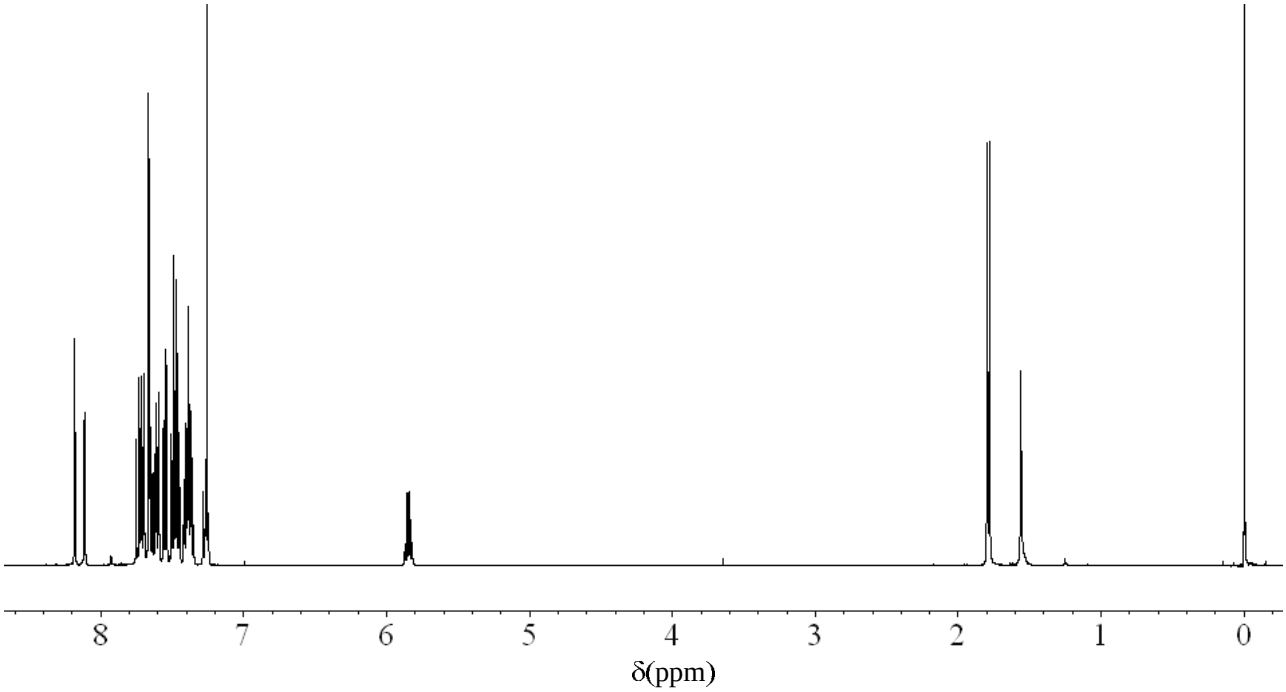


Figure S8. ^{1}H NMR spectrum of **4** in $CDCl_3$.

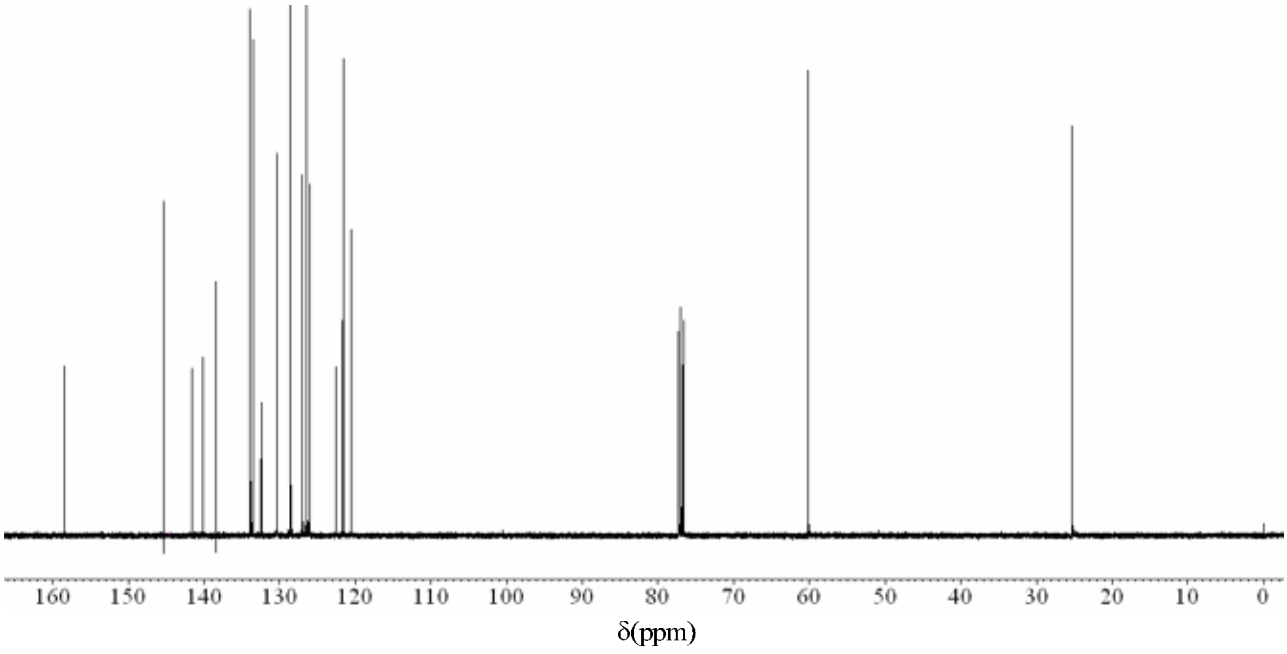


Figure S9. ^{13}C NMR spectrum of **1R** in $CDCl_3$.

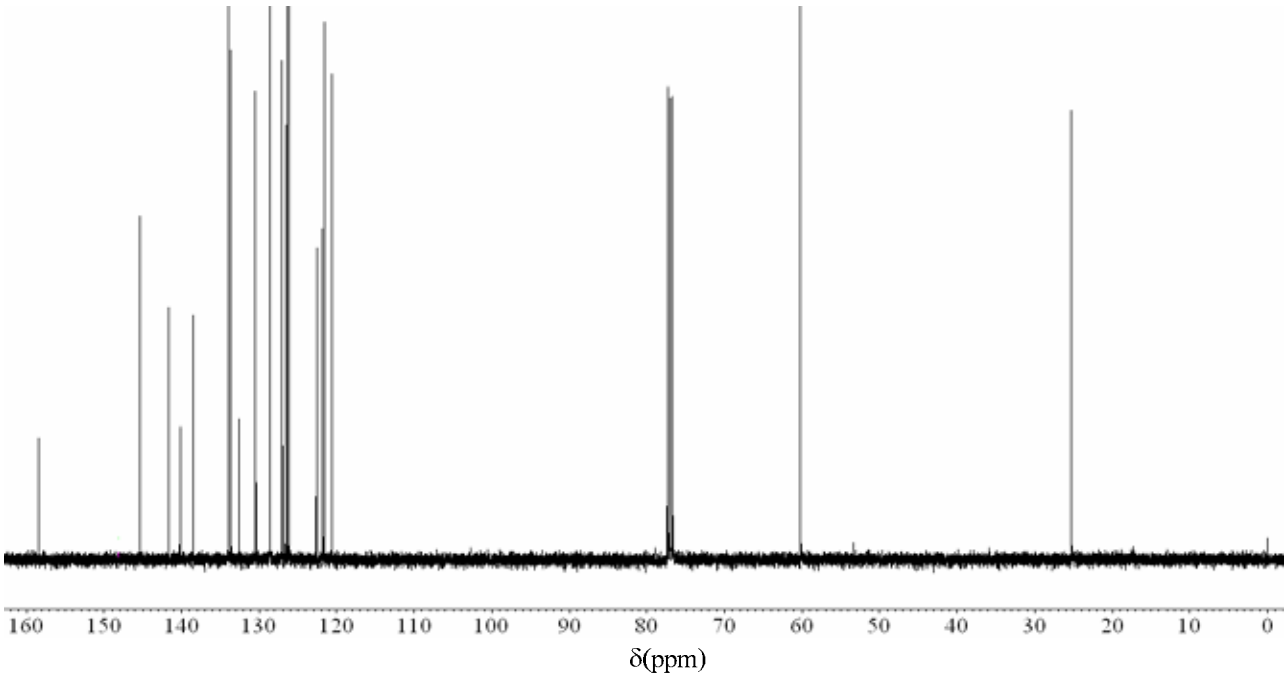


Figure S10. ^{13}C NMR spectrum of **1S** in $CDCl_3$.

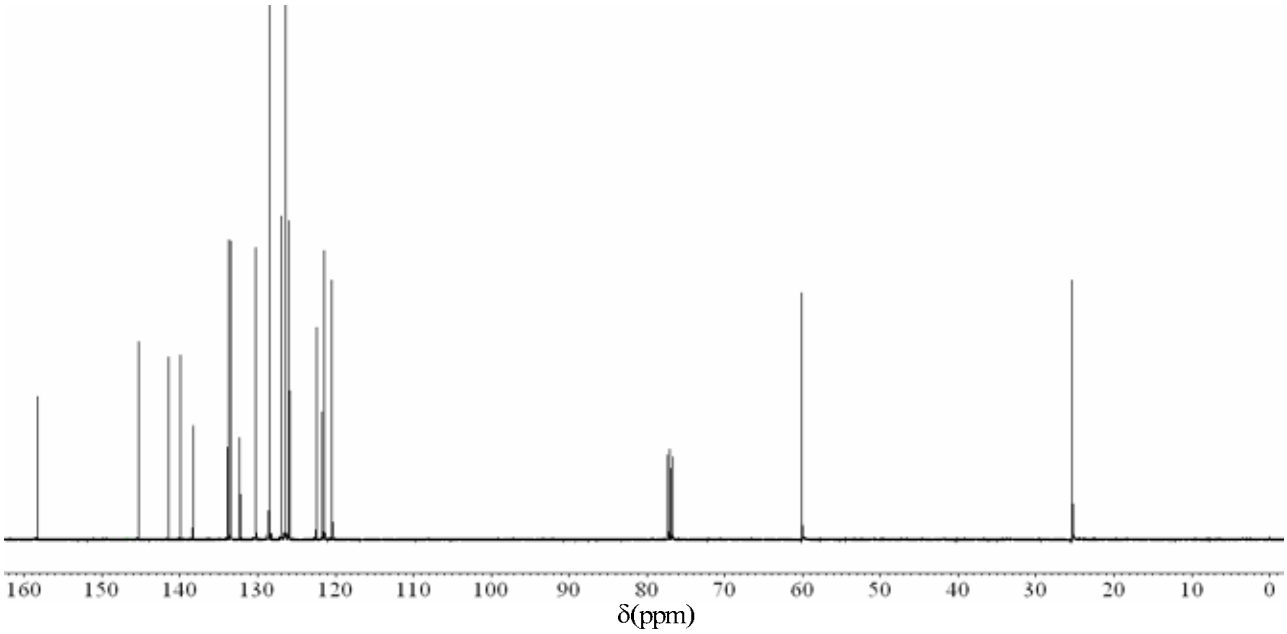


Figure S11. ^{13}C NMR spectrum of **1rac** in $CDCl_3$.

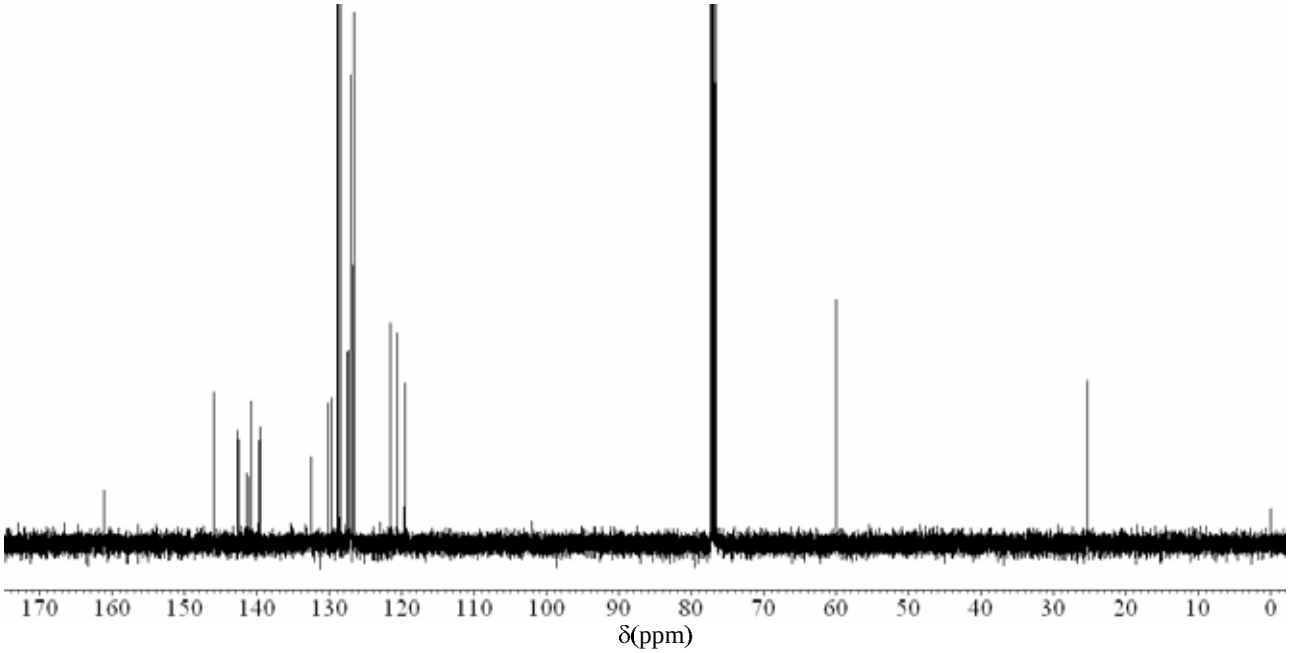


Figure S12. ^{13}C NMR spectrum of **4** in $CDCl_3$.

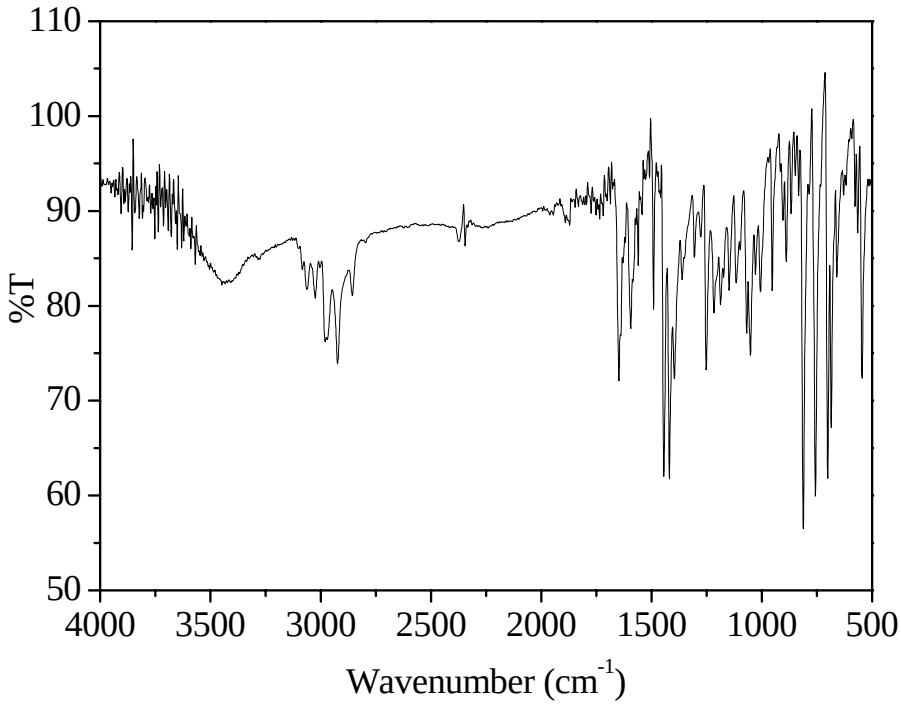


Figure S13. FT-IR spectrum of **1R**.

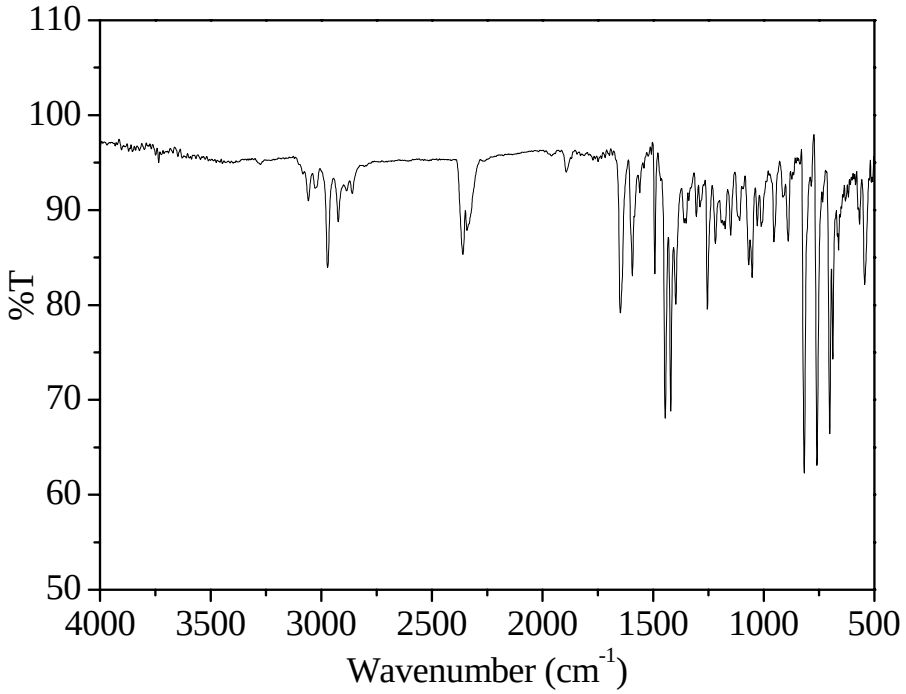


Figure S14. FT-IR spectrum of **1S**.

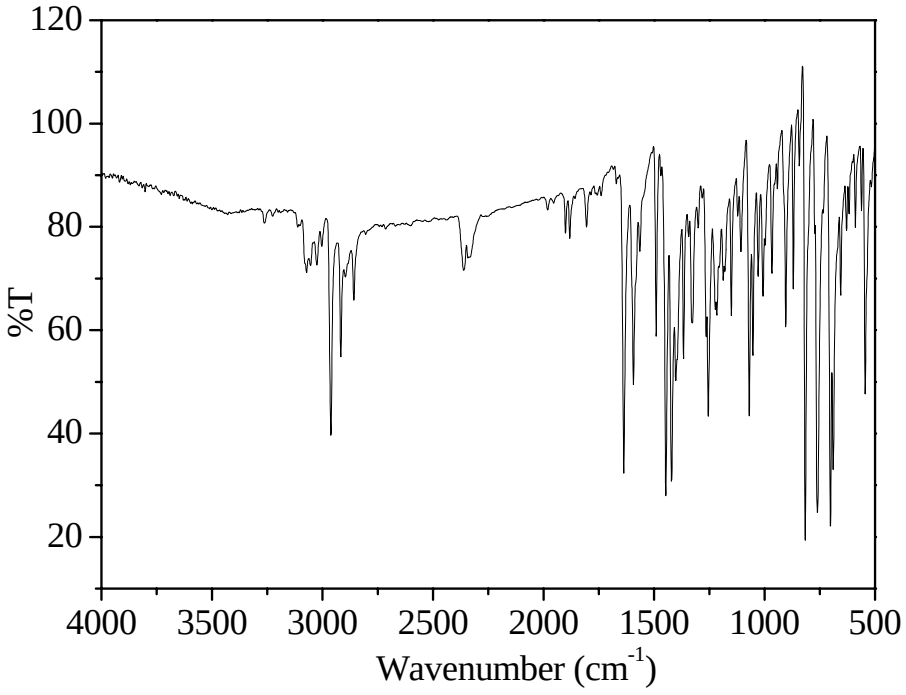


Figure S15. FT-IR spectrum of **1rac**.

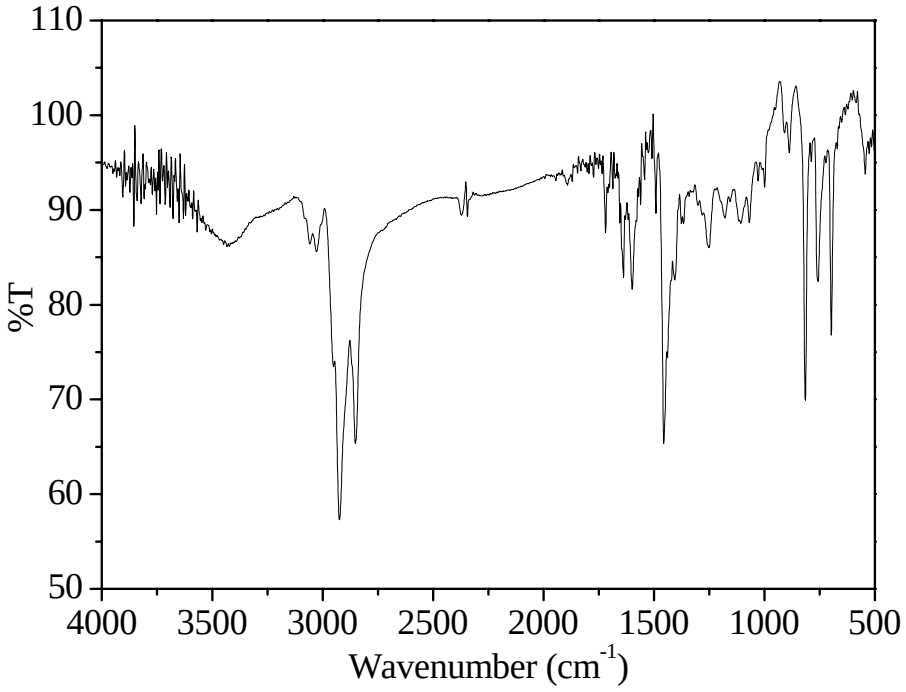


Figure S16. FT-IR spectrum of **2R**.

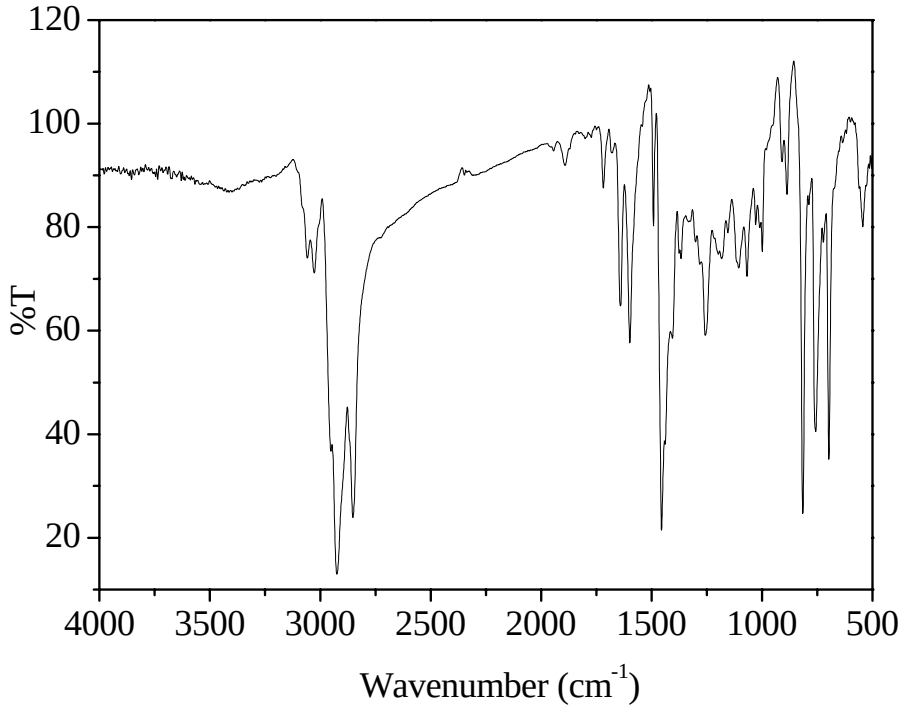


Figure S17. FT-IR spectrum of **2S**.

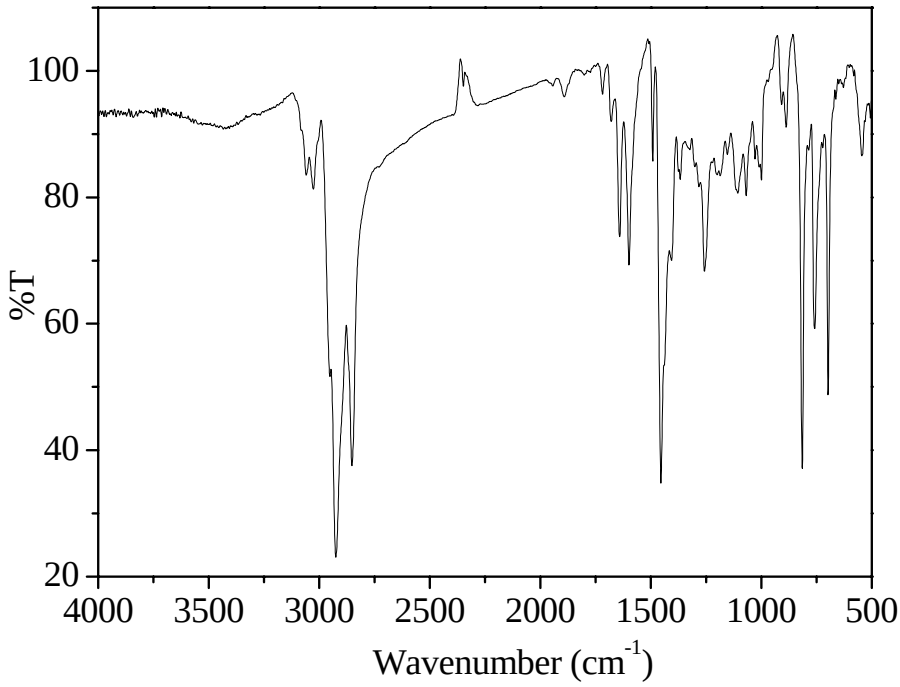


Figure S18. FT-IR spectrum of **2rac**.

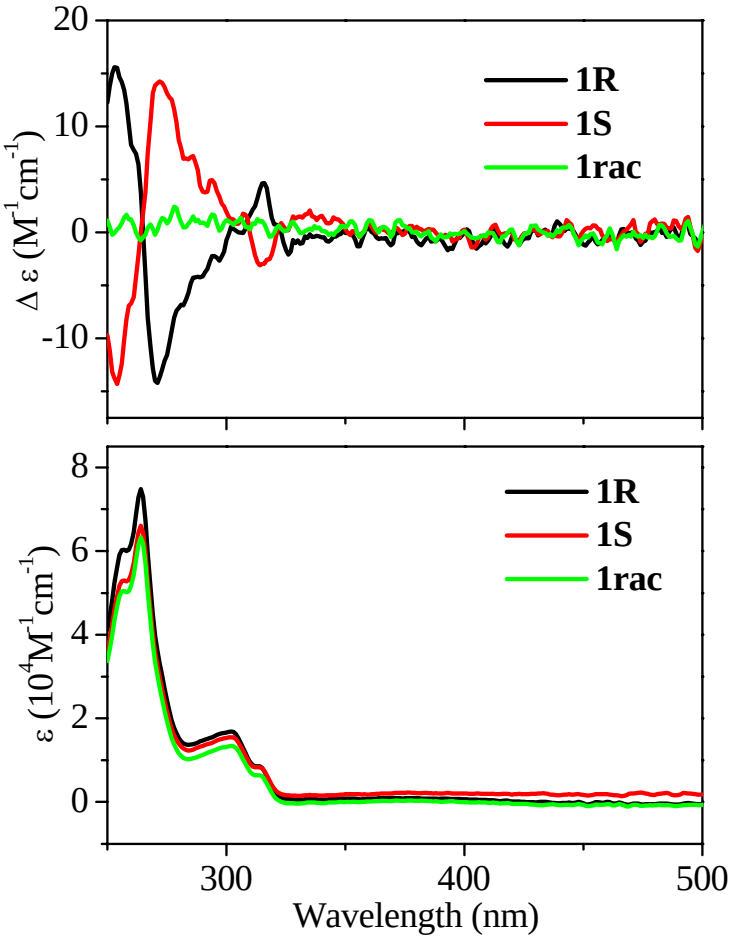


Figure S19. CD and UV-vis spectra of monomers in 10^{-5} M THF solution.

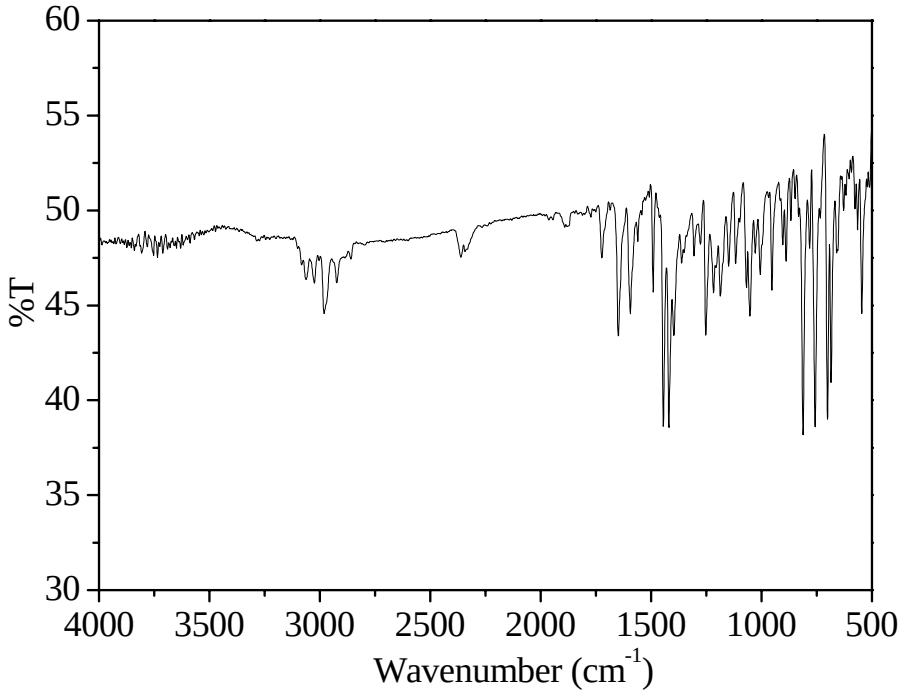


Figure S20. IR spectrum of 5% of 2,7-dibromofluorenone & 95 % of **1R**.

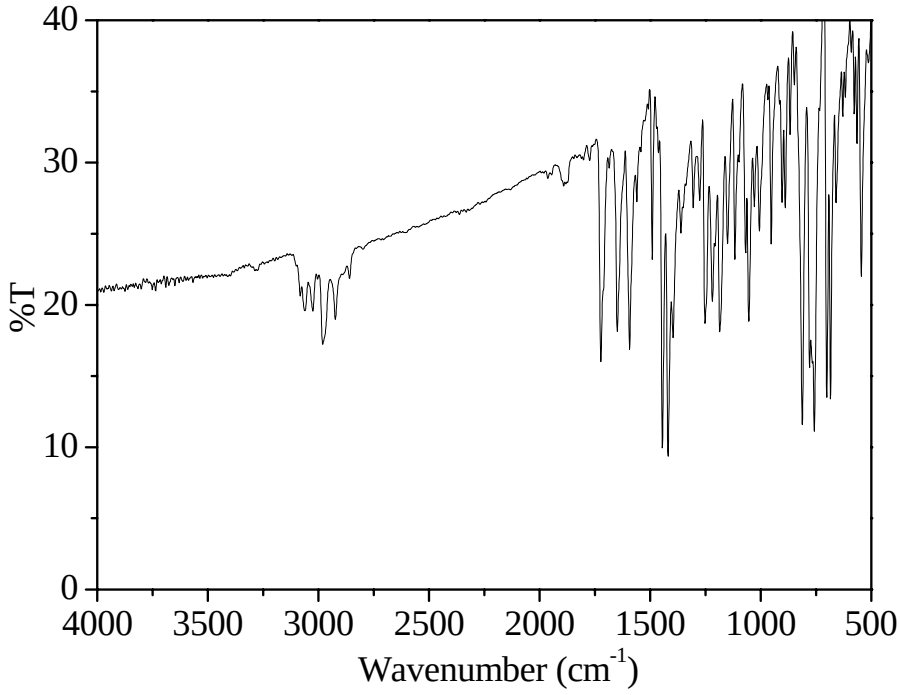


Figure S21. IR spectrum of 10 % of 2,7-dibromofluorenone & 90% of **1R**.

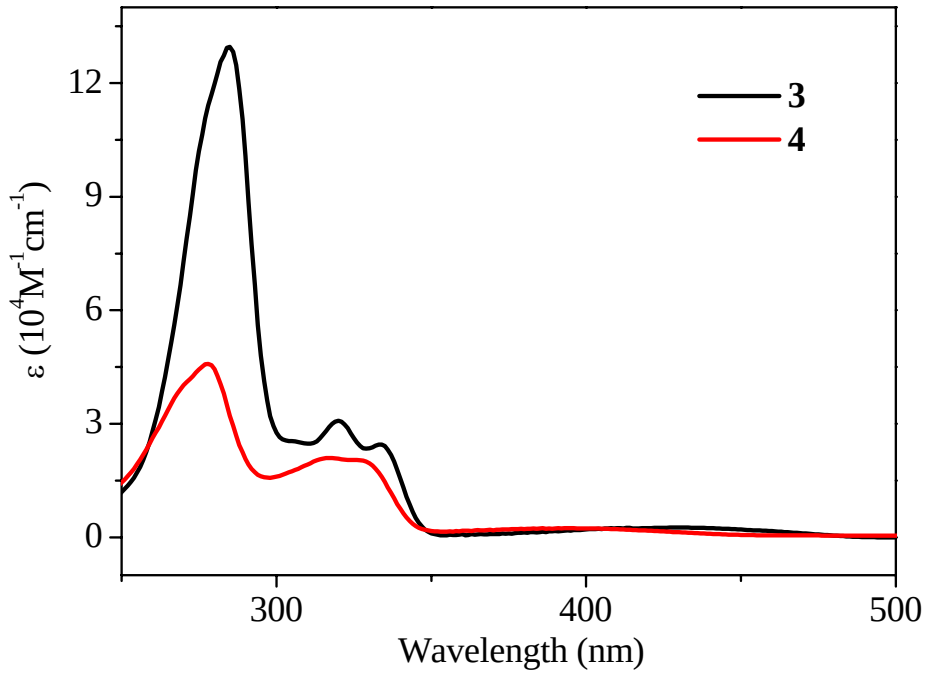


Figure S22. UV-vis spectra of **3** and **4** in 10^{-5} M THF solution.

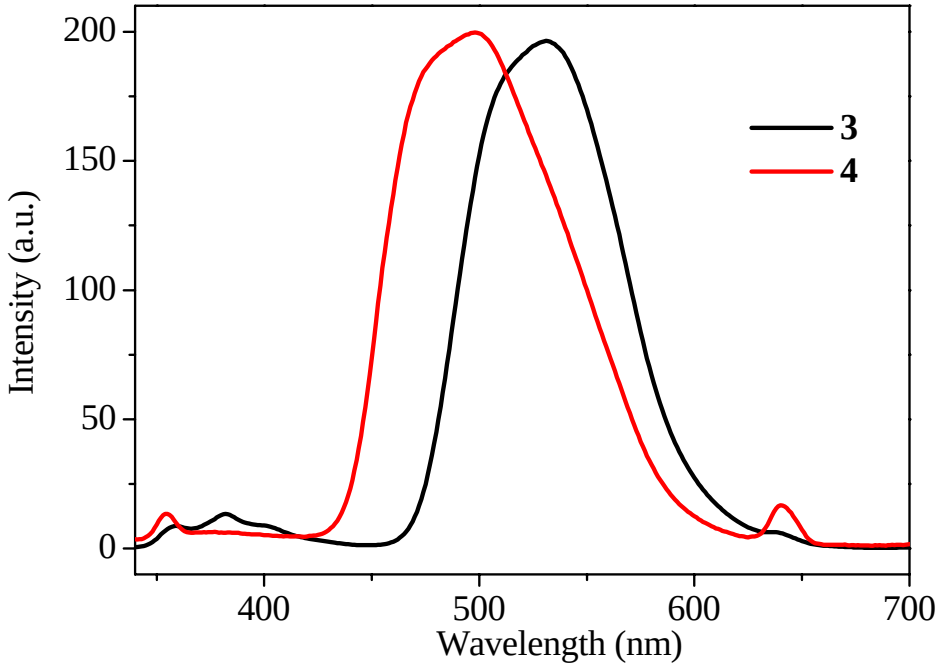


Figure S23. Fluorescence spectra of **3** and **4** in 10^{-5} M THF solution. (λ_{ex} = 320 nm)

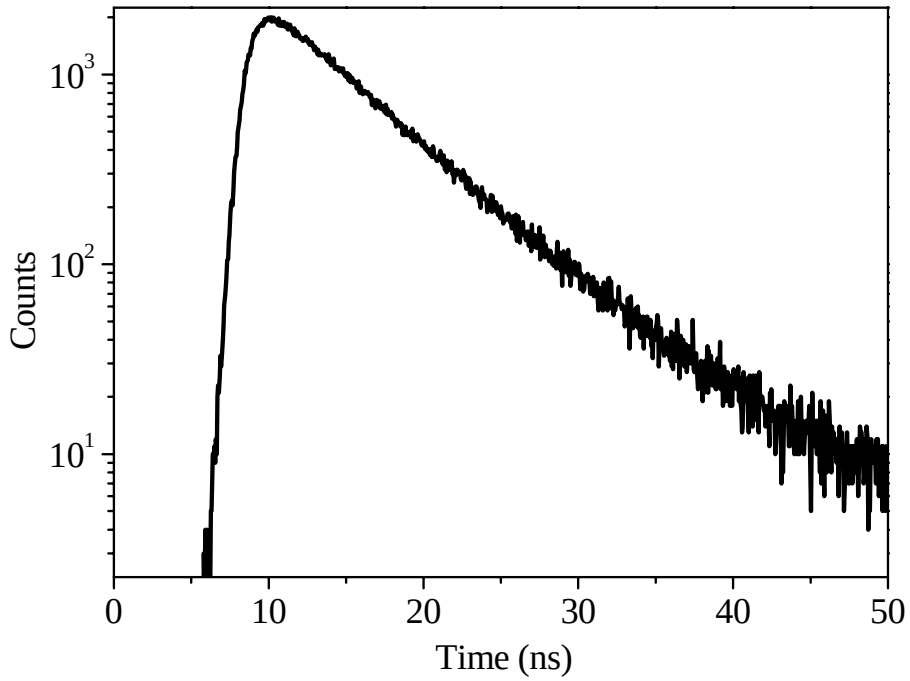


Figure S24. Fluorescence decay curves of **2R** in 10^{-5} M THF solution (λ_{ex} = 370 nm).

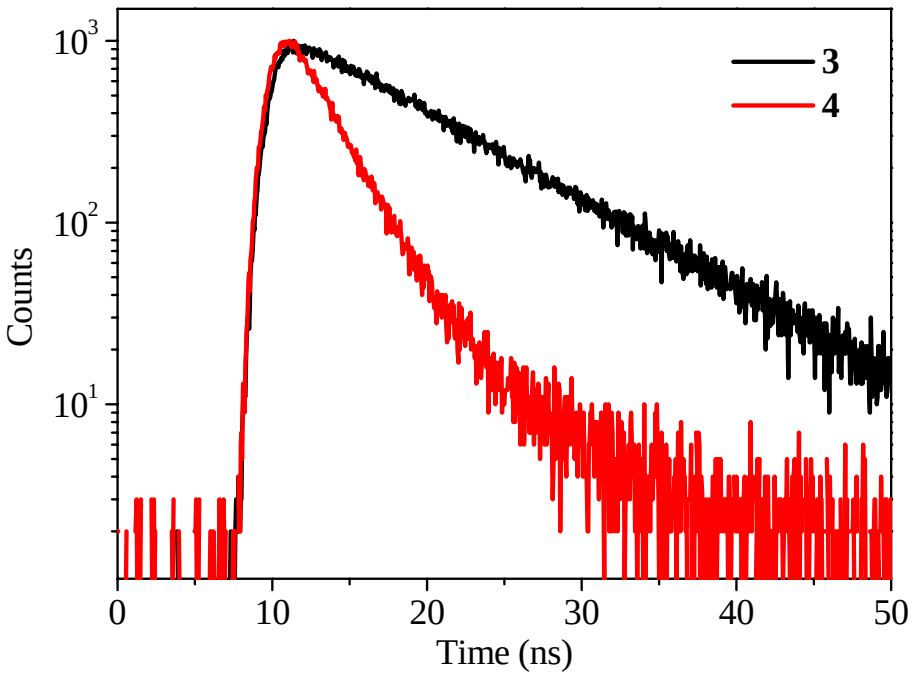


Figure S25. Fluorescence decay curves of **3** and **4** in 10^{-5} M THF solution (λ_{ex} = 320 nm).

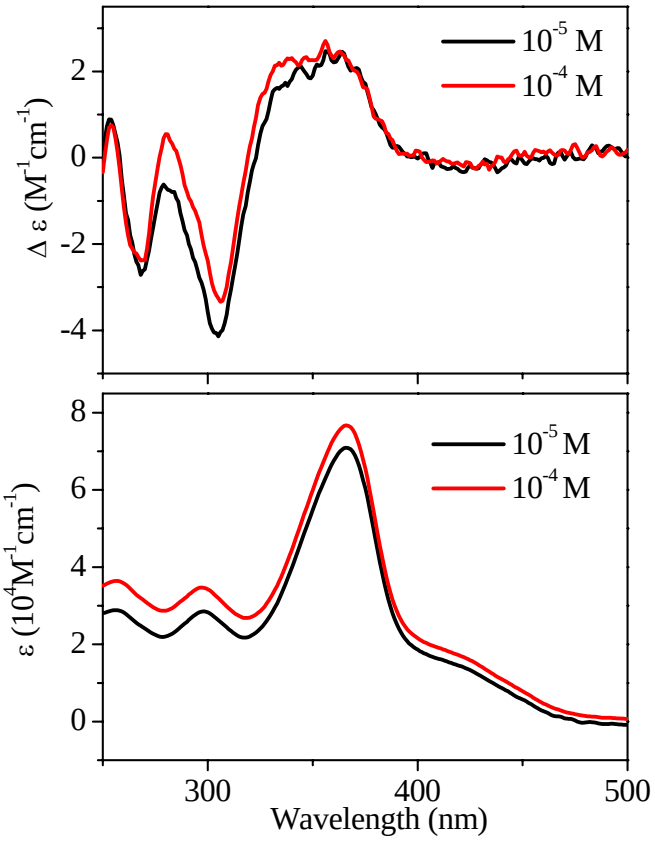

10-5 M
10-4 M
Δ ε (M-1cm-1)
2
0
-2
-4
10-5 M
10-4 M
ε (10⁴M-1cm-1)
8
6
4
2
0
300
400
500
Wavelength (nm)

Figure S26. CD & UV-vis spectra of **2R** at two concentrations in THF.

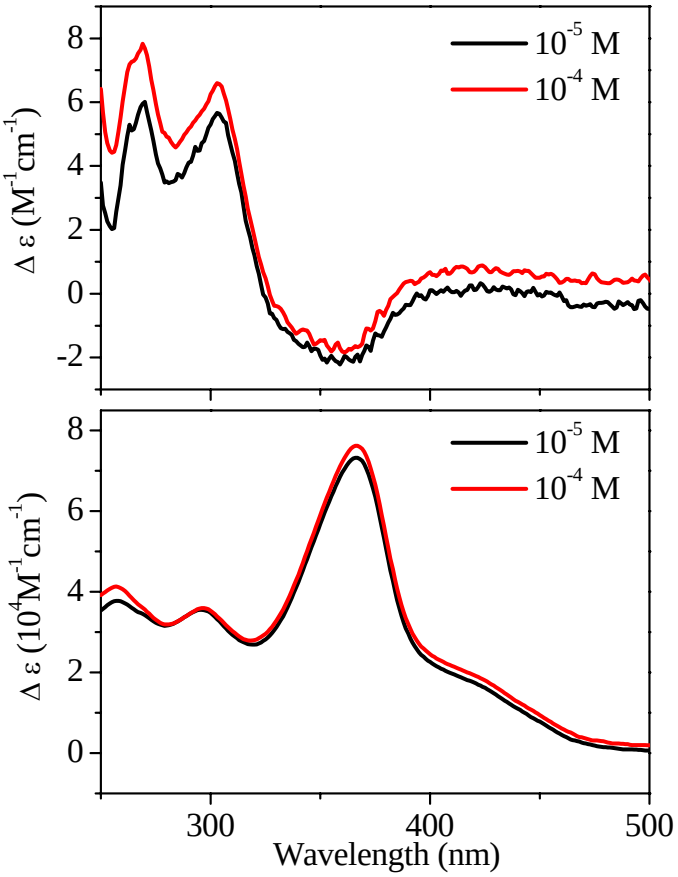


Figure 27. CD & UV-vis spectra of **2S** at two concentrations in THF solution.

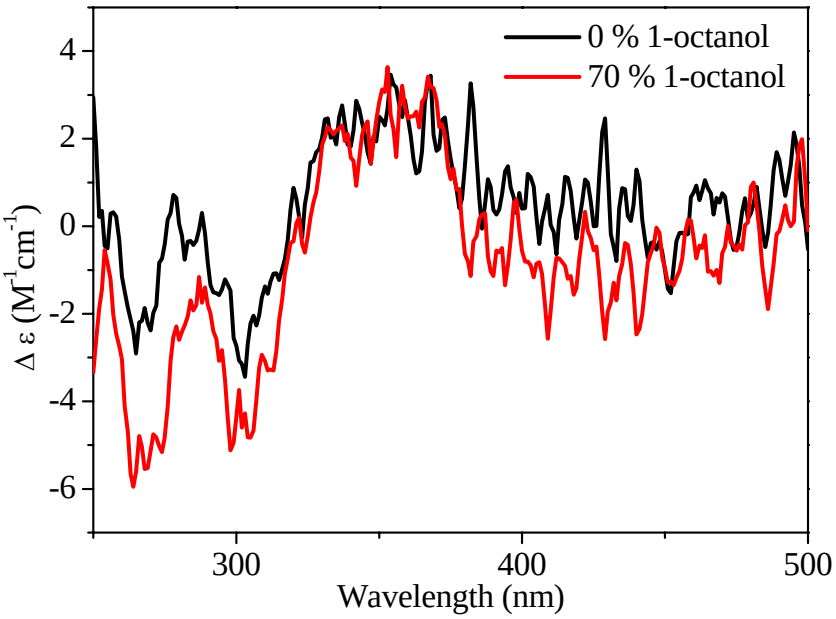


Figure 28. CD spectra of **2R** in 10^{-5} M co-solvent (THF / 1-octanol = 3 : 7).

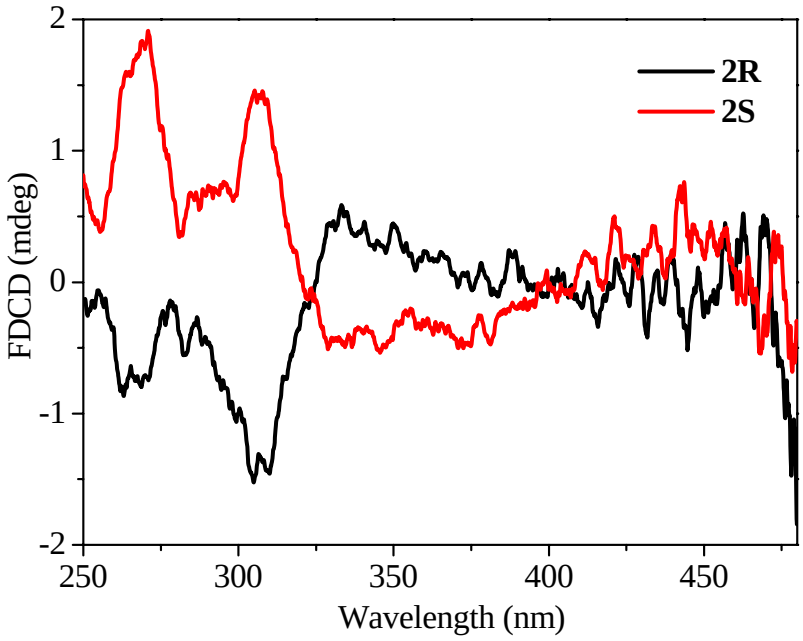


Figure S29. FDCD spectra of **2R** and **2S** in 10^{-5} M THF solution.

Molecular orbital calcinations were carried out using Gaussian 03 program.

Table S1: Cartesian coordinate for **4** optimized at B3LYP/6-31G(d)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-2.846505	0.295256	0.351948
2	6	0	-2.453686	-0.678158	0.087136
3	6	0	-1.495660	-3.261613	-0.471043
4	6	0	-1.082285	-0.906358	0.005554
5	6	0	-3.368344	-1.730484	-0.125807
6	6	0	-2.867642	-3.012345	-0.408174
7	6	0	-0.603458	-2.214834	-0.262263
8	1	0	-3.565112	-3.823212	-0.597661
9	1	0	-1.135616	-4.264447	-0.685218
10	6	0	0.866105	-2.208164	-0.243573
11	6	0	3.605015	-1.592228	-0.069796
12	6	0	1.295394	-0.900604	0.044236
13	6	0	1.805459	-3.216658	-0.445754
14	6	0	3.162475	-2.899479	-0.354645
15	6	0	2.641969	-0.583769	0.128610

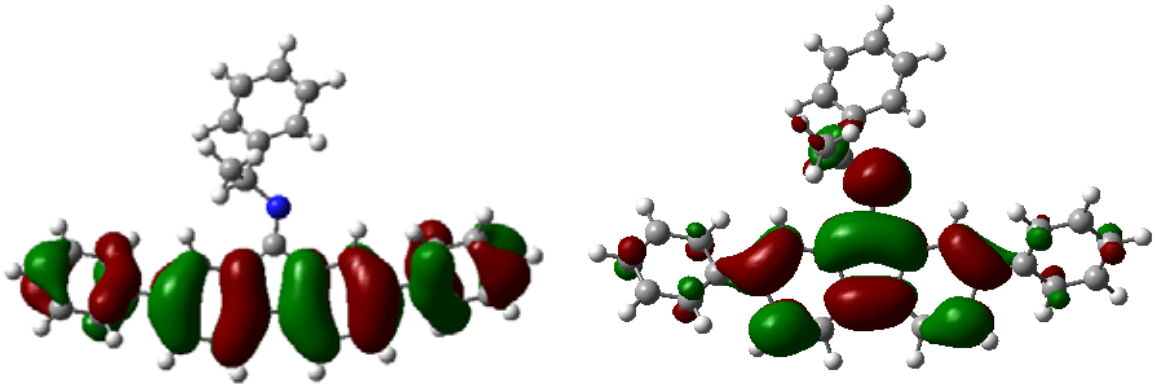
16	1	0	1.500073	-4.237230	-0.661707
17	1	0	3.898626	-3.687843	-0.482879
18	1	0	2.939885	0.442021	0.321606
19	6	0	0.110574	-0.006258	0.189495
20	7	0	0.264993	1.245450	0.401233
21	6	0	-0.846272	2.179316	0.512365
22	1	0	-1.703593	1.862530	-0.096835
23	6	0	-1.293666	2.253828	1.989844
24	1	0	-0.451098	2.556626	2.619432
25	1	0	-1.654416	1.280060	2.338527
26	1	0	-2.094831	2.990832	2.107594
27	6	0	-0.423290	3.558728	0.013924
28	6	0	0.278049	6.150782	-0.819605
29	6	0	-1.364331	4.390108	-0.604148
30	6	0	0.877456	4.039413	0.204638
31	6	0	1.225050	5.325826	-0.209012
32	6	0	-1.020107	5.678187	-1.017299
33	1	0	-2.376906	4.025201	-0.767722
34	1	0	1.615357	3.388610	0.662124
35	1	0	2.240538	5.683633	-0.058028
36	1	0	-1.763565	6.307999	-1.499323
37	1	0	0.551398	7.151343	-1.144374
38	6	0	5.055042	-1.285245	0.019803
39	6	0	7.808905	-0.699021	0.194305
40	6	0	5.540585	-0.369235	0.968990
41	6	0	5.981142	-1.899548	-0.840873
42	6	0	7.342099	-1.610759	-0.754287
43	6	0	6.901213	-0.079067	1.055066
44	1	0	4.846601	0.099990	1.660706
45	1	0	5.626641	-2.588608	-1.602455
46	1	0	8.038028	-2.092090	-1.436517
47	1	0	7.253718	0.626984	1.802473
48	1	0	8.869668	-0.473047	0.261407
49	6	0	-4.830502	-1.484394	-0.046052
50	6	0	-7.607826	-1.015786	0.105896
51	6	0	-5.693134	-2.432720	0.530467
52	6	0	-5.391614	-0.296074	-0.544820
53	6	0	-6.764041	-0.063746	-0.468972
54	6	0	-7.065759	-2.201760	0.604743
55	1	0	-5.279264	-3.346485	0.947943
56	1	0	-4.748651	0.438973	-1.021248
57	1	0	-7.175844	0.859037	-0.869169
58	1	0	-7.711883	-2.946249	1.062498
59	1	0	-8.677693	-0.835319	0.164550

Table S2. TD-DFT results for **4**.

First Excited State 3.052 eV 406 nm f = 0.110
HOMO ->LUMO 0.673

Second Excited State 3.557 eV 349 nm f = 0.004
HOMO-5 -> LUMO 0.49655
HOMO-3 -> LUMO 0.12815
HOMO-2 -> LUMO 0.25768
HOMO-1 -> LUMO -0.34187

Third Excited State 3.895 eV 318 nm f = 0.437
HOMO-8 -> LUMO -0.25021
HOMO-4 -> LUMO 0.11213
HOMO-2 -> LUMO 0.19202
HOMO-1 -> LUMO 0.16500
HOMO -> LUMO+1 0.56435



HOMO(-5.600 eV) LUMO(-1.918 eV)

Figure S30. HOMO and LUMO for **4**.

The observed fluorescence may be derived form the first excited state. The absorption band is corresponded to CT band. The intramolecular CT structure may be formed after irradiation. By using this hypothesis, it is reasonable to explain the large Stokes shift of the imino-fluorene chromophore **4.**

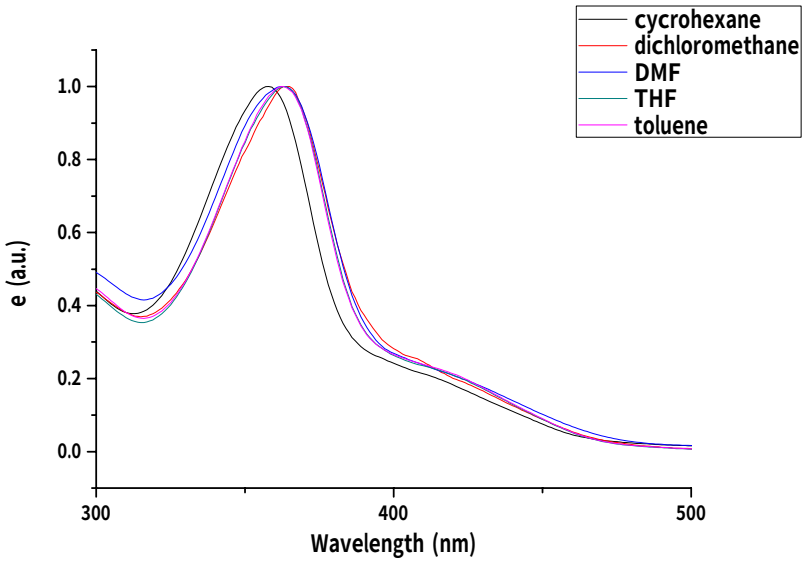


Figure S31. UV-vis spectra of **2** in several solvents.