Supplementary Information

Light-Emitting Property of Simple AIE Compounds in Gel, Suspension and Precipitates, and Application to Quantitative Determination of Enantiomer Composition

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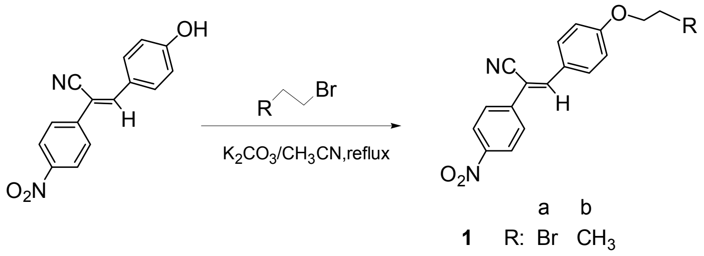
Materials and Methods

Materials. All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and were used as received.

Measurements

Fluorescent emission spectra were collected on Shimadzu RF-5301 fluorophotometer at 298 K. In the experimental of determination of enantiomer purity, the samples were standing for 4 h after mixing all compounds in solvent(s) and vigorously shaken for about 2 minutes until they became a good suspension before measuring the fluorescence intensity. T_g was measured by using the tube inversion technique at a heating speed of 2 ^{o}C per minute. Field emission scanning electron microscopy (FE-SEM) images were taken on a FEI Sirion200 electron microscope operating at 5 kV or 10 kV. Mass spectrum was measured on Bruker BioApex FTMS instrument.

Synthesis of 1a and 1b



Synthesis of 1a. To the flask were added (*E*)-α-(*p*-nitrophenyl)-β-(*p*-hydroxyphenyl) acrylonitrile (1.06 g, 4 mmol), 1,2-dibromoethane (1.7 ml, 20 mmol), anhydrous K_2CO_3 (0.61 g, 4.4 mmol) and dry acetonitrile (30 ml) in order. The mixture was refluxed for about 6 h until one of reactants disappeared (monitored by TLC, ethyl acetate/petroleum ether 1:3). The reaction mixture was cooled to room temperature and the resultant yellow precipitates were collected by filtering. The solid was dissolved into chloroform and washed with water until the organic phase had pH 6. Upon dried over anhydrous Na_2SO_4 and filtered, the organic phase was concentrated under reduced pressure to give a yellow solid. The crude product was recrystallized from acetonitrile to get yellow product **1a** 1.28g, 86%. Mp 159 – 160 ^{o}C; IR (KBr) ν 3103, 3069, 2210, 1577, 1509, 1460, 1421, 1372, 1337, 1309 cm^{-1}; ^{1}H NMR (400 MHz , $CDCl_3$) δ 8.31 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.8 Hz, 2H), 7.63 (s, 1H), 7.04 (d, J = 8.8 Hz, 2H), 4.40 (t, J = 6.4 Hz, 2H), 3.70 (t, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 147.6, 144.8, 140.9, 132.0, 126.4, 126.3, 124.3, 117.6, 115.2, 106.8, 67.9, 28.6; ESI-MS m/z calcd for $C_{17}H_{13}BrN_2O_3$ 372 [M], found 372 [M]. Anal. Calcd for $C_{17}H_{13}BrN_2O_3$: C 54.71, H 3.51, N 7.51. Found: C 55.65, H 3.58, N 7.57.

Synthesis of 1b. The preparation procedure of **1b** was the same as that for **1a**, gave yellow solid in 77% yield. Mp 145 – 146 ^{o}C; IR (KBr) ν 2967, 2934, 2881, 2209, 1668, 1577, 1510, 1465, 1430, 1375, 1337 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.8 Hz, 2H), 7.60 (s, 1H), 6.99 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 1.88 – 1.60 (m, 2H), 1.06 (t, J = 7.2 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 162.1, 147.5, 145.1, 141.2, 132.0, 126.3, 125.4, 124.3, 117.8, 115.1, 105.9, 69.8, 22.4, 10.5; ESI-MS m/z calcd for $C_{18}H_{16}N_2O_3$ 308 [M], found 308 [M]. Anal. Calcd for $C_{18}H_{16}N_2O_3$: C 70.12, H 5.23, N 9.09. Found: C 70.23, H 5.31, N 9.02.

Supporting Figures

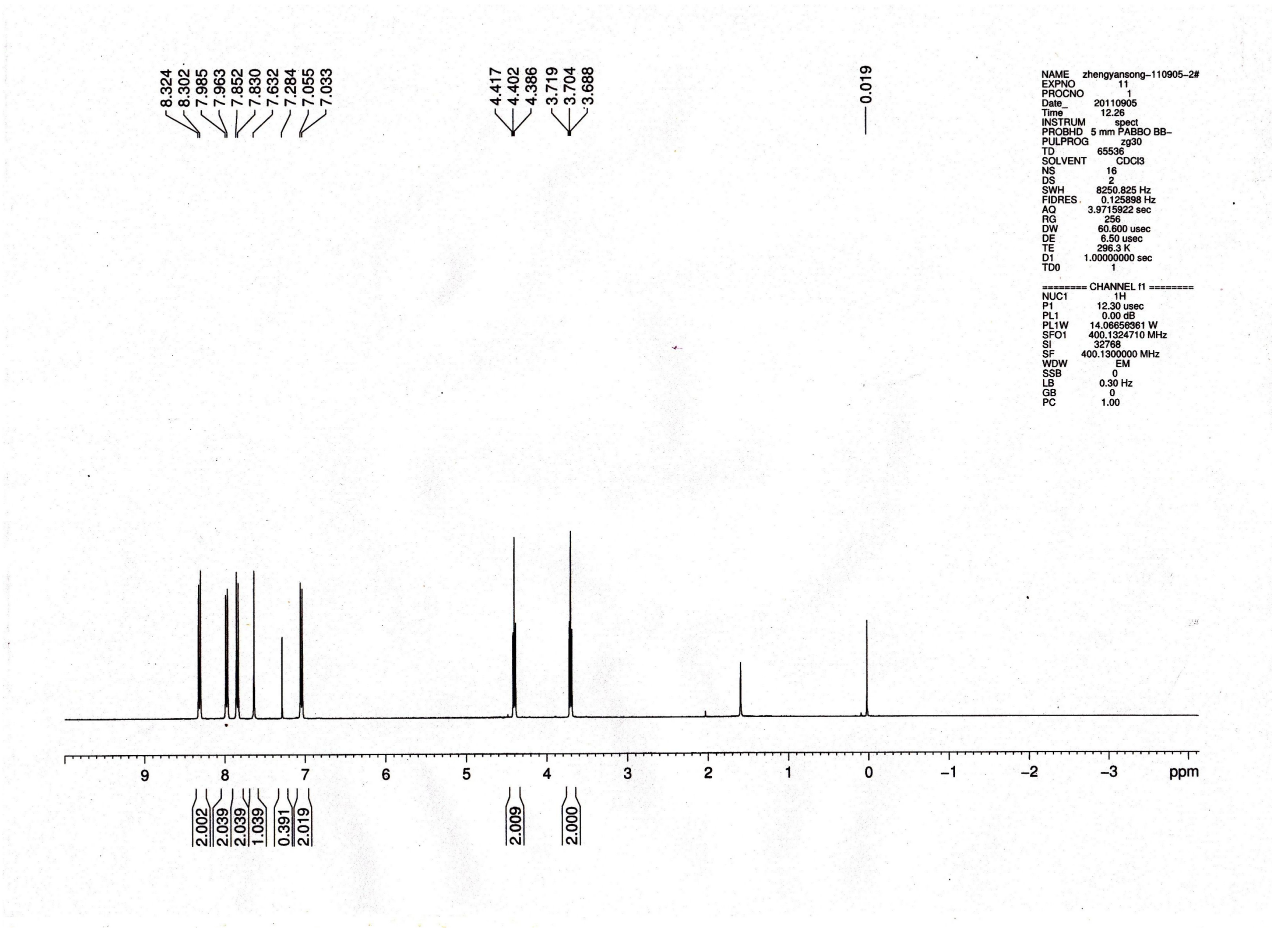


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Figure S1. ^{1}H NMR spectrum of **1a** in $CDCl_3$.

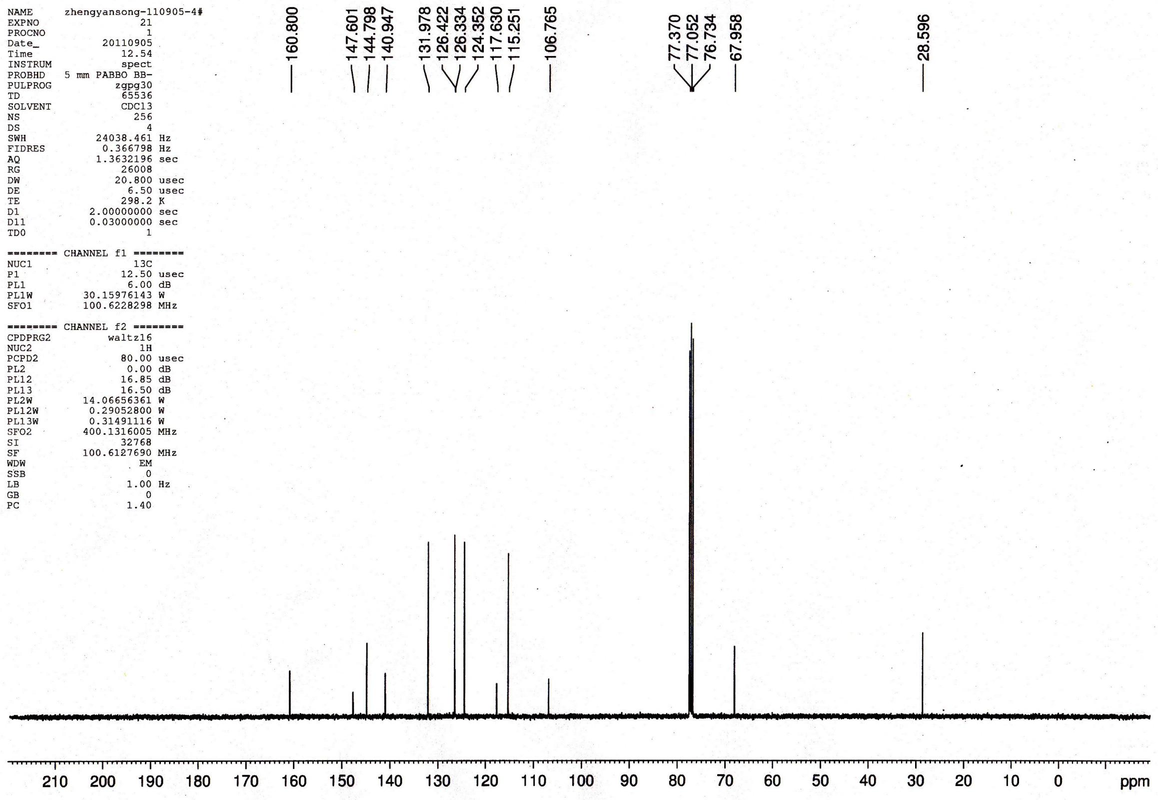

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Figure S2. ^{13}C NMR spectrum of **1a** in $CDCl_3$.

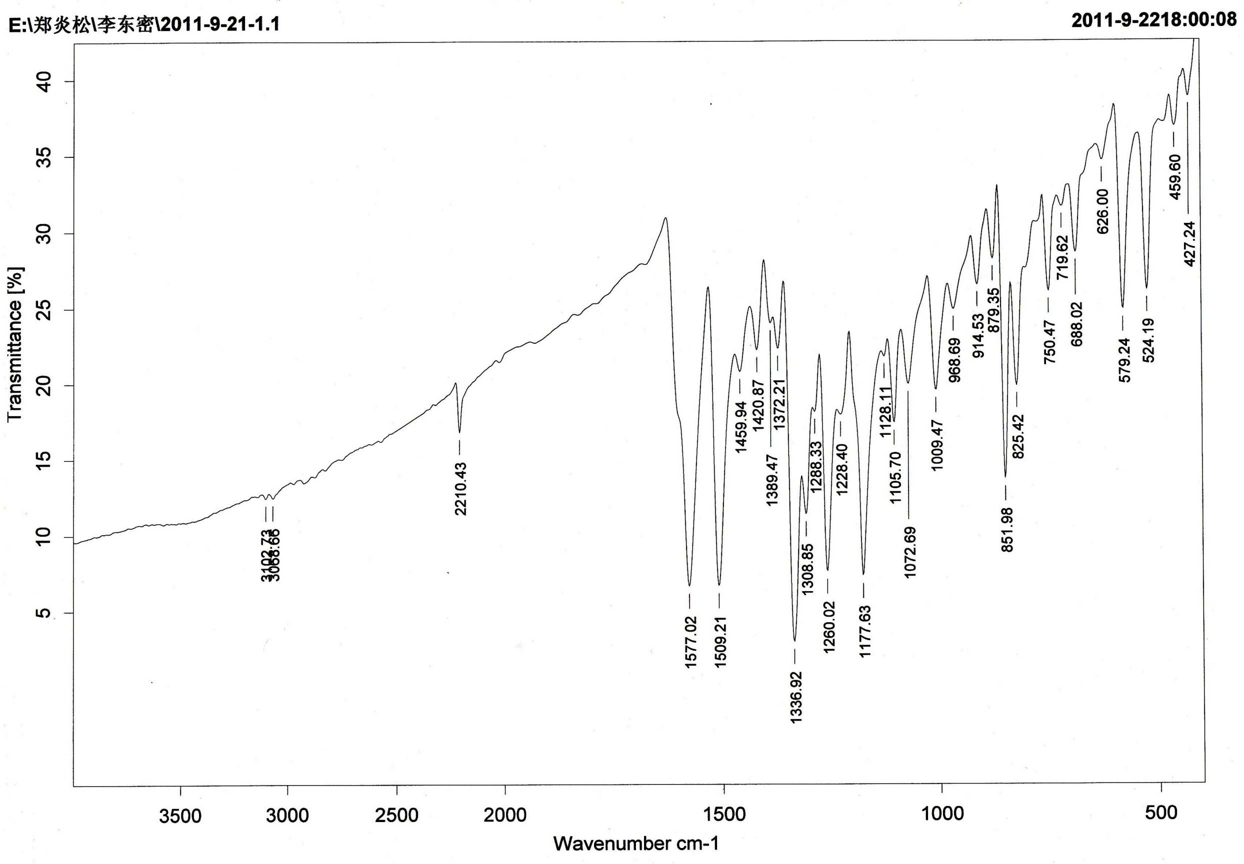

Figure S3. IR spectrum of **1a**.

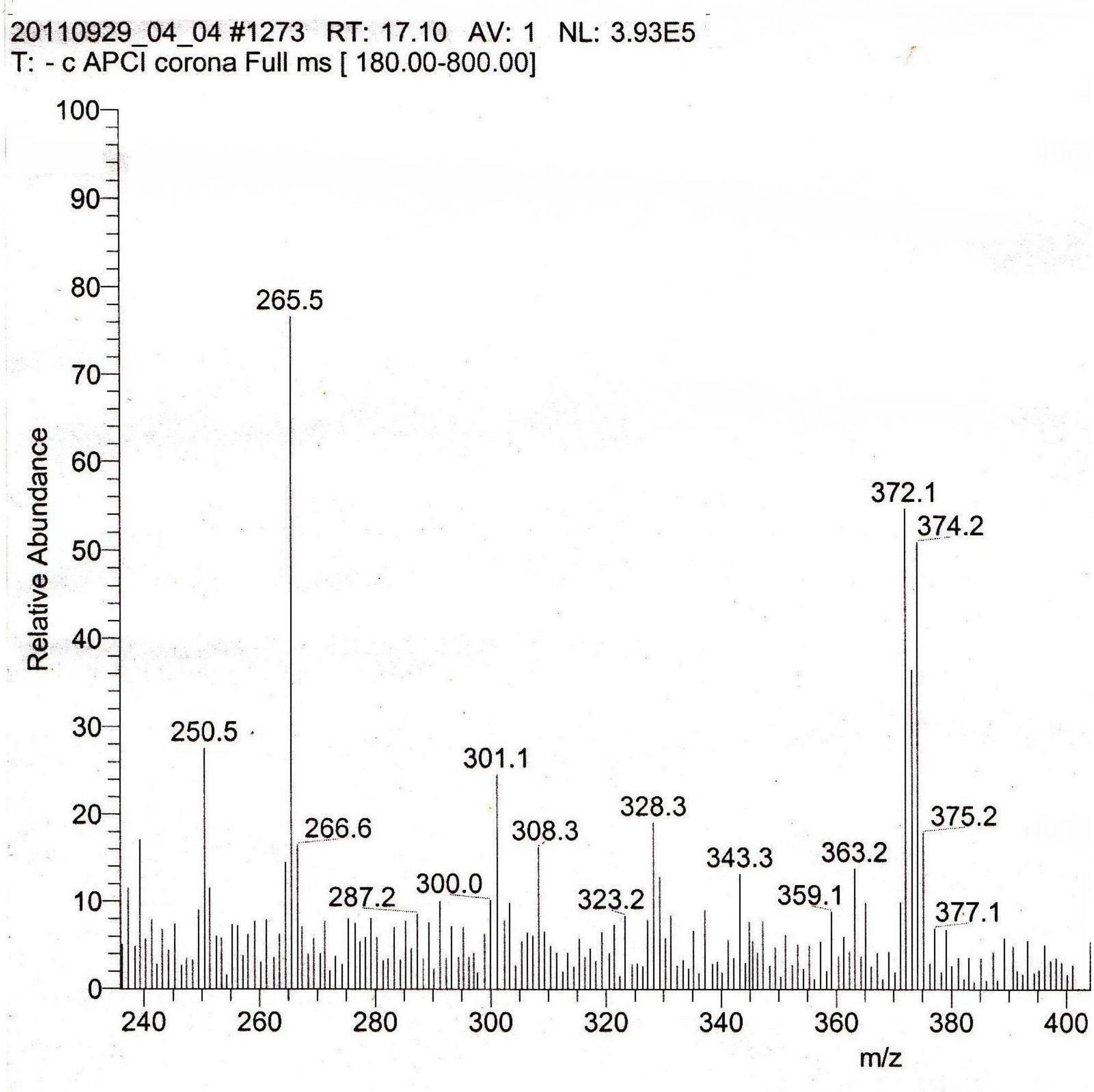

Figure S4. MS spectrum of **1a**.

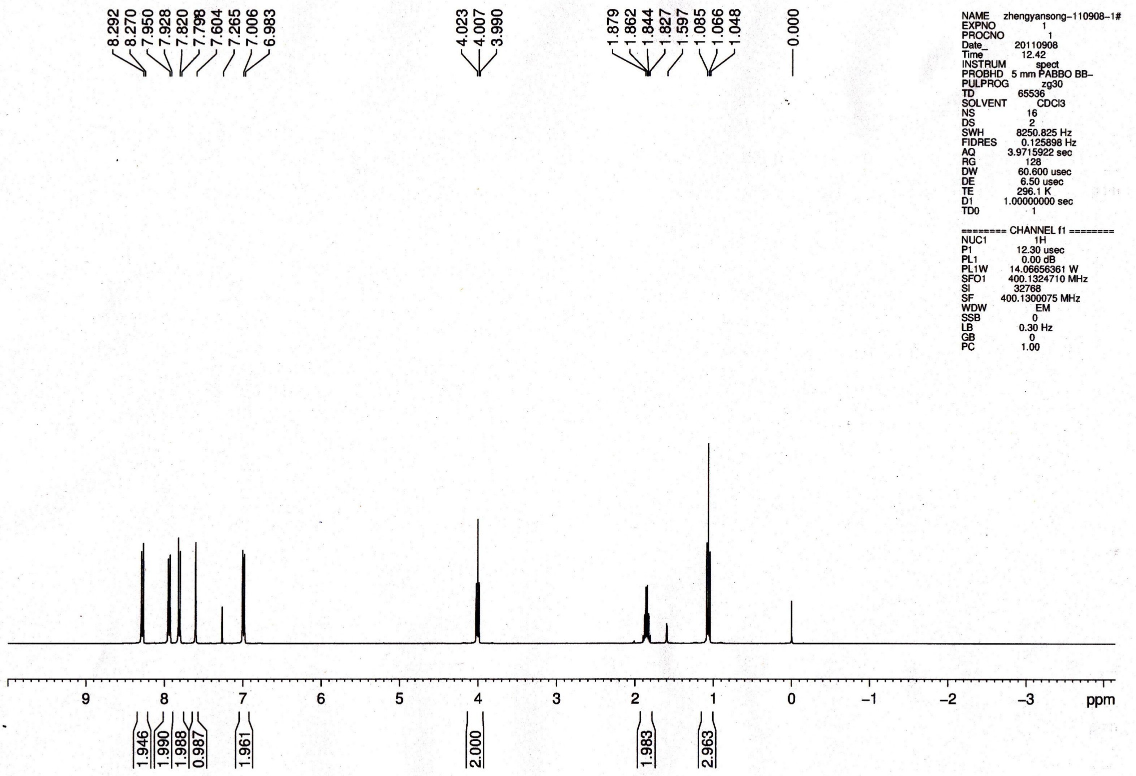

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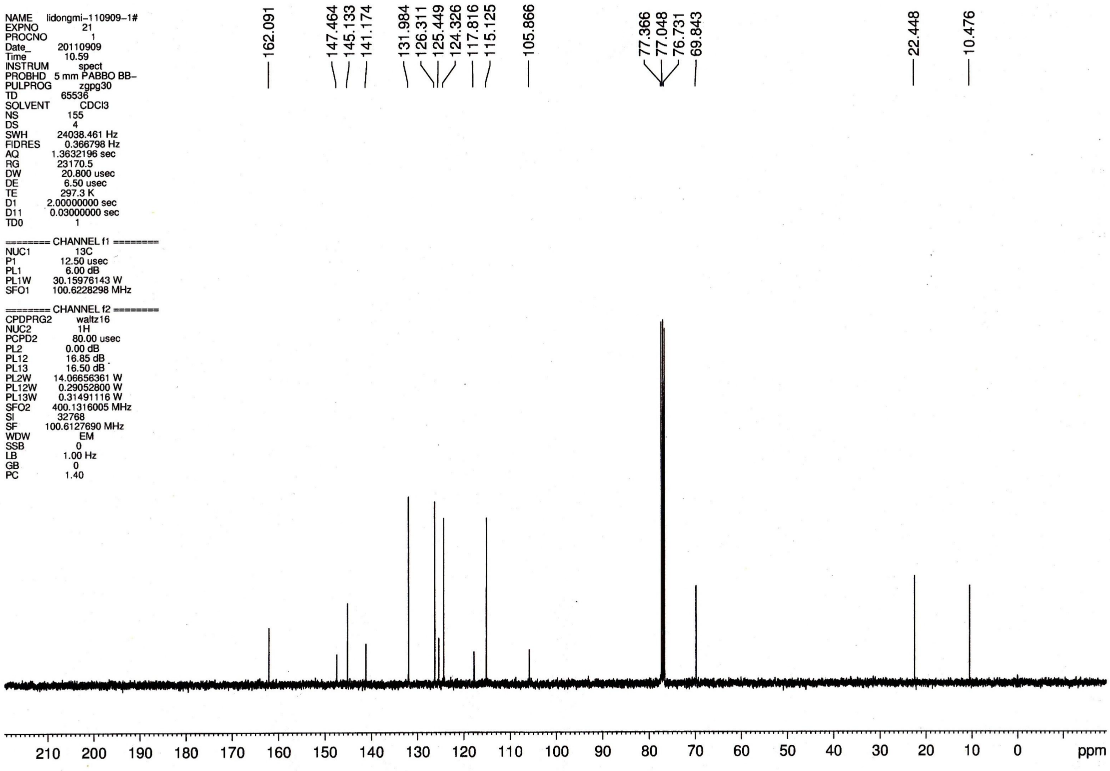
Figure S5. ^{1}H NMR spectrum of **1b** in $CDCl_3$.



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TE            297.3 K
D1       2.00000000 sec
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PL13W     0.31491116 W
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Figure S6. ^{13}C NMR spectrum of **1b** in CDCl$_3$.

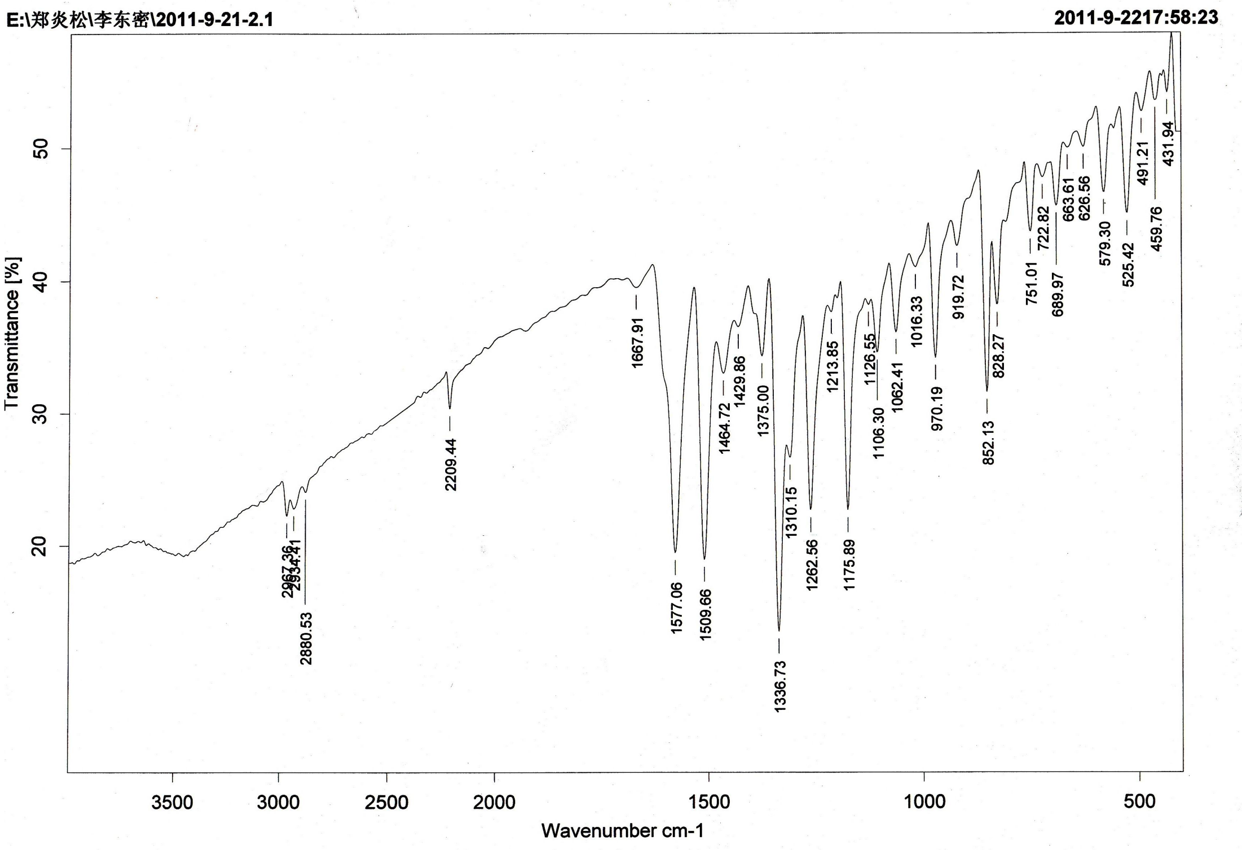

Figure S7. IR spectrum of **1b**.

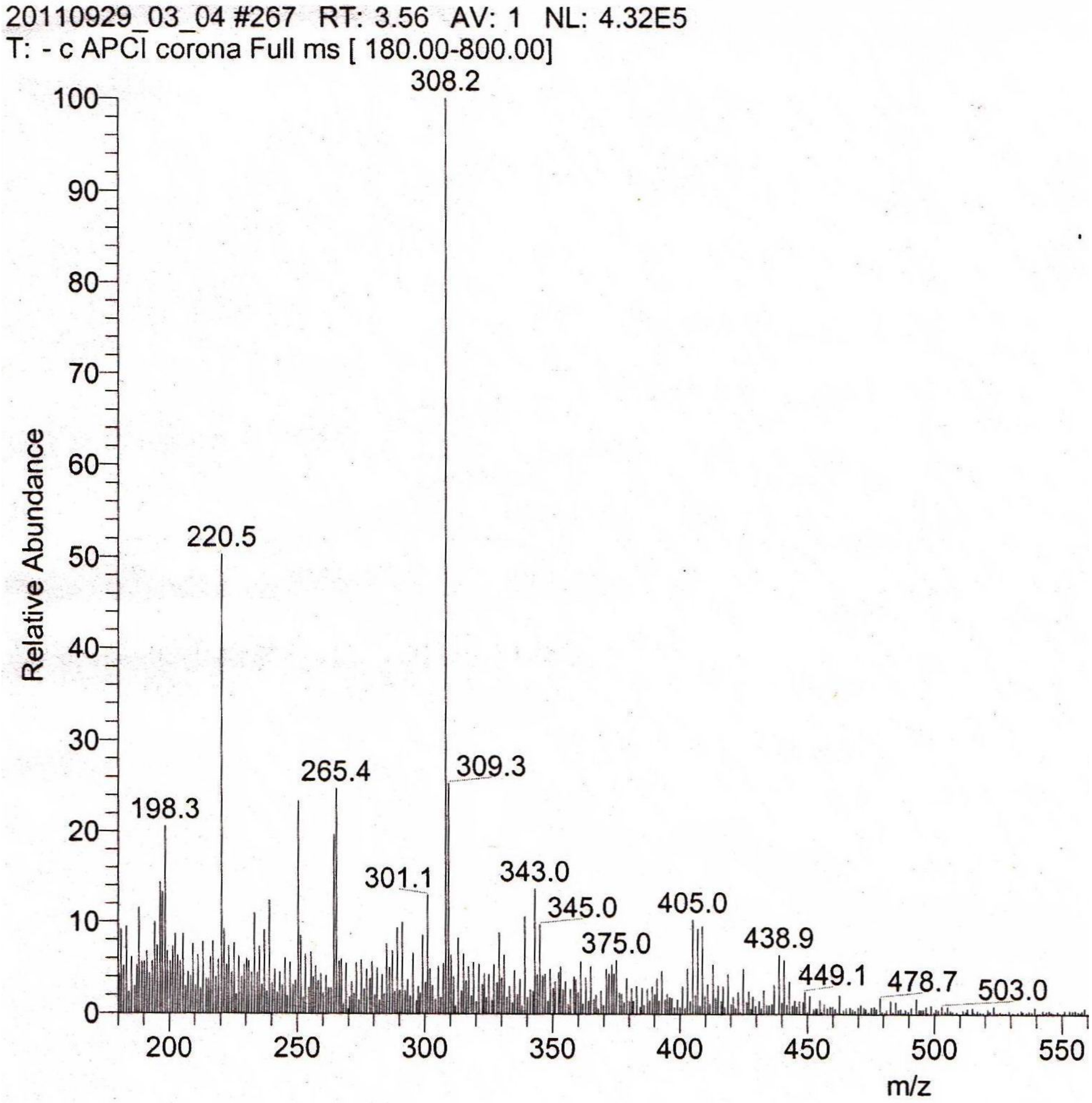

Figure S8. MS spectrum of **1b**.

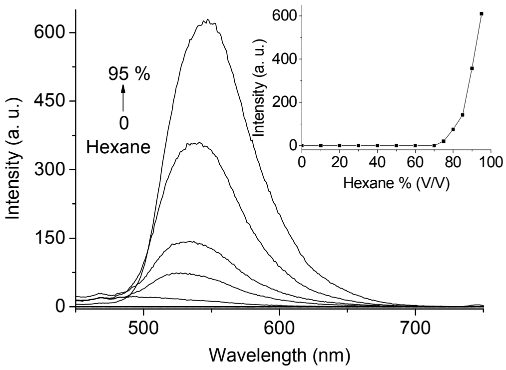

Figure S9. Change of fluorescence spectra of **1a** (2.0×10^{-3} M) with increasing content of hexane in 1,2-dichloroethane. λ_{ex} = 370 nm, ex/em slits = 5/5 nm, Inset, curve of fluorescence intensity at λ_{max} = 540 nm changed with hexane percent.

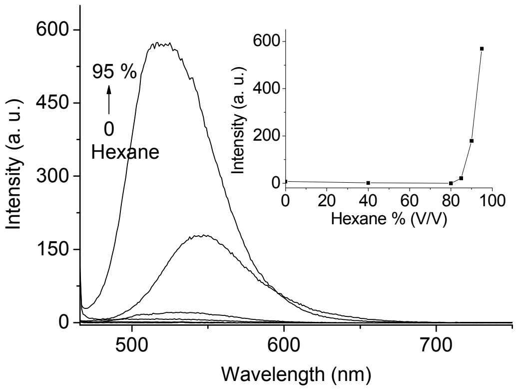

Figure S10. Change of fluorescence spectra of **1b** (2.0×10^{-3} M) with increasing content of hexane in 1,2-dichloroethane. λ_{ex} = 460 nm, ex/em slits = 3/3 nm, Inset, curve of fluorescence intensity at λ_{max} = 523 nm changed with hexane percent.

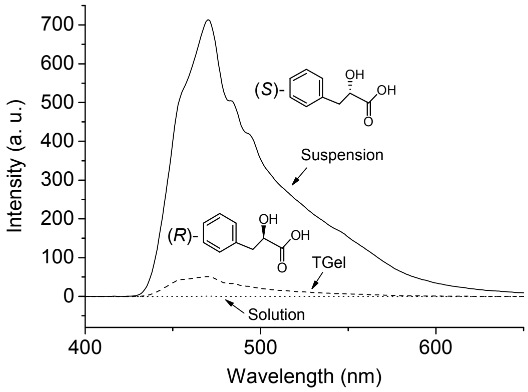

Figure S11. The fluorescence spectra of **1a** in the mixture of the enantiomer of phenyllactic acids and (*1S,2R*)-**3**. Solid line, that in the suspension from mixture of (*1S,2R*)-**3** and (*S*)-phenyllactic acid; dash line, that in the transparent gel (TGel) from mixture of (*1S,2R*)-**3** and (*R*)-phenyllactic acid; dot line, that in solution obtained by heating the TGel. The fluorescence intensity ratio resulted from two enantiomers of the acid (I_S/I_R) was 14. [(*1S,2R*)-**3**] = [acid] = 5[**1a**] = 10 mM in 1,2-dichloroethane.

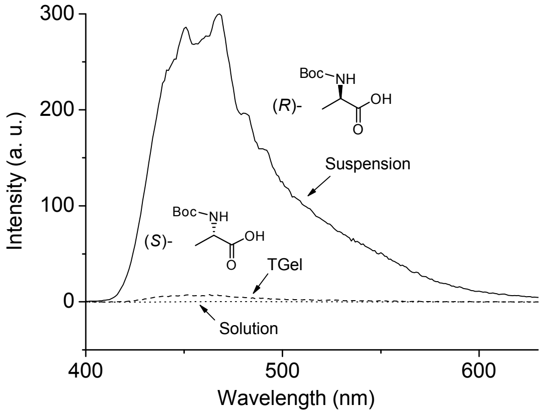

Figure S12. The fluorescence spectra of **1a** in the mixture of the enantiomer of N-Boc-alanine and (*1S,2R*)-**3**. Solid line, that in the suspension from mixture of (*1S,2R*)-**3** and (*S*)-N-Boc-alanine; dash line, that in the transparent gel (TGel) from mixture of (*1S,2R*)-**3** and (*R*)- N-Boc-alanine; dot line, that in solution obtained by heating the TGel. The fluorescence intensity ratio resulted from two enantiomers of the acid (I_R/I_S) was 23. [(*1S,2R*)-**3**] = [acid] = 5[**1a**] = 10 mM in 1,2-dichloroethane.

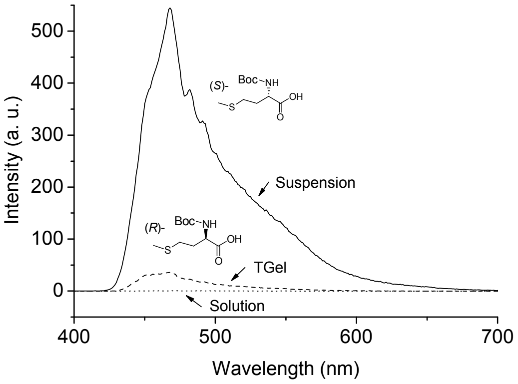

Figure S13. The fluorescence spectra of **1a** in the mixture of the enantiomer of N-Boc-methionine and (*1S,2R*)-**3**. Solid line, that in the suspension from mixture of (*1S,2R*)-**3** and (*S*)-N-Boc-methionine; dash line, that in TGel from mixture of (*1S,2R*)-**3** and (*R*)-N-Boc-methionine; dot line, that in solution obtained by heating the TGel. The fluorescence intensity ratio resulted from two enantiomers of the acid (I_S/I_R) was 15. [(*1S,2R*)-**3**] = [acid] = 5[**1a**] = 10 mM in 1,2-dichloroethane.

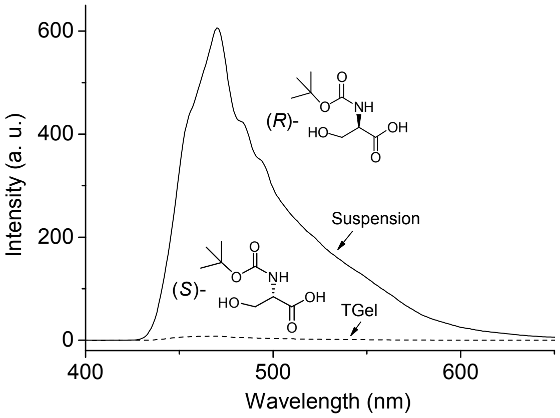

Figure S14. The fluorescence spectra of **1a** in the mixture of the enantiomer of N-Boc-serine and (*1S,2R*)-**3**. Solid line, that in the suspension from mixture of (*1S,2R*)-**3** and (*R*)-N-Boc-serine; dashed line, that in TGel from mixture of (*1S,2R*)-**3** and (*S*)-N-Boc-serine; dot line, that in solution obtained by heating the TGel. The fluorescence intensity ratio resulted from two enantiomers (I_R/I_S) was 78. [(*1S,2R*)-**3**] = [acid] = 5[**1a**] = 10 mM in 1,2-dichloroethane.

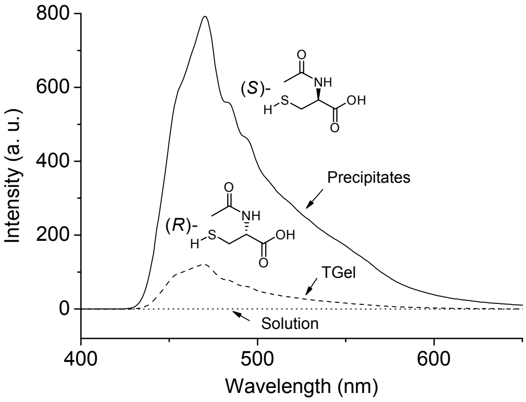

Figure S15. The fluorescence spectra of **1a** in the mixture of the enantiomer of N-acetylcysteine and (*1S,2R*)-**3**. Solid line, that in the precipitates from mixture of (*1S,2R*)-**3** and (*S*)-N-acetylcysteine; dash line, that in the transparent gel from mixture of (*1S,2R*)-**3** and (*R*)-N-acetylcysteine; dot line, that in solution obtained by heating the TGel. The fluorescence intensity ratio resulted from two enantiomers (I_S/I_R) was 6.6. [(*1S,2R*)-**3**] = [acid] = 5[**1a**] = 10 mM in 1,2-dichloroethane.

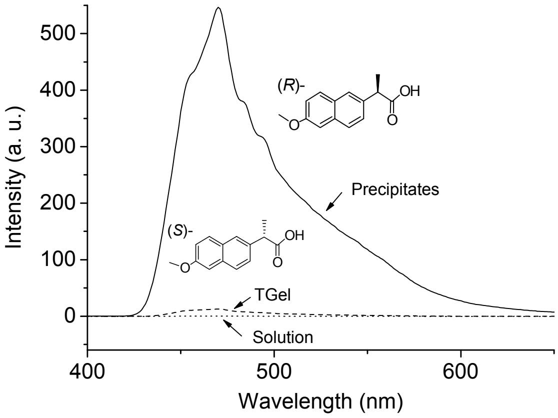

Figure S16. The fluorescence spectra of **1a** in the mixture of the enantiomer of Naproxen and (*1S,2R*)-**3**. Solid line, that in the precipitates from mixture of (*1S,2R*)-**3** and (*R*)-Naproxen; dashed line, that in the transparent gel from mixture of (*1S,2R*)-**3** and (*S*)-Naproxen; dot line, that in solution obtained by heating the TGel. The fluorescence intensity ratio resulted from two enantiomers (I_R/I_S) was 46. [(*1S,2R*)-**3**] = [acid] = 5[**1a**] = 10 mM in 1,2-dichloroethane.

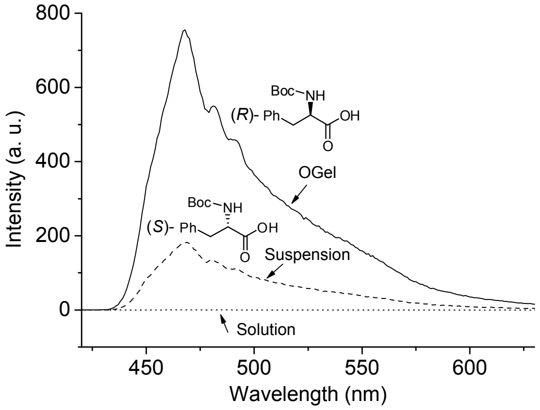

Figure S17. The fluorescence spectra of **1a** in the mixture of the enantiomer of N-Boc-phenylalanine and (*1S,2R*)-**3**. Solid line, that in the opaque gel (OGel) from mixture of (*1S,2R*)-**3** and (*R*)-N-Boc-phenylalanine; dashed line, that in the suspension from mixture of (*1S,2R*)-**3** and (*S*)-N-Boc-phenylalanine; dot line, that in solution obtained by heating the OGel. The fluorescence intensity ratio resulted from two enantiomers (I_R/I_S) was 4.2. [(*1S,2R*)-**3**] = [acid] = 5[**1a**] = 10 mM in 1,2-dichloroethane.

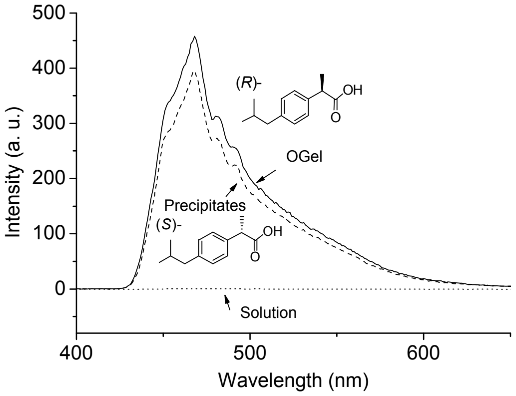

Figure S18. The fluorescence spectra of **1a** in the mixture of the enantiomer of Ibuprofen and (*1S,2R*)-**3**. Solid line, that in OGel from mixture of (*1S,2R*)-**3** and (*R*)-Ibuprofen; dashed line, that in the precipitates from mixture of (*1S,2R*)-**3** and (*S*)-Ibuprofen; dot line, that in solution obtained by heating OGel. The fluorescence intensity ratio resulted from two enantiomers (I_R/I_S) was 1.2. [(*1S,2R*)-**3**] = [acid] = 5[**1a**] = 10 mM in 1,2-dichloroethane.

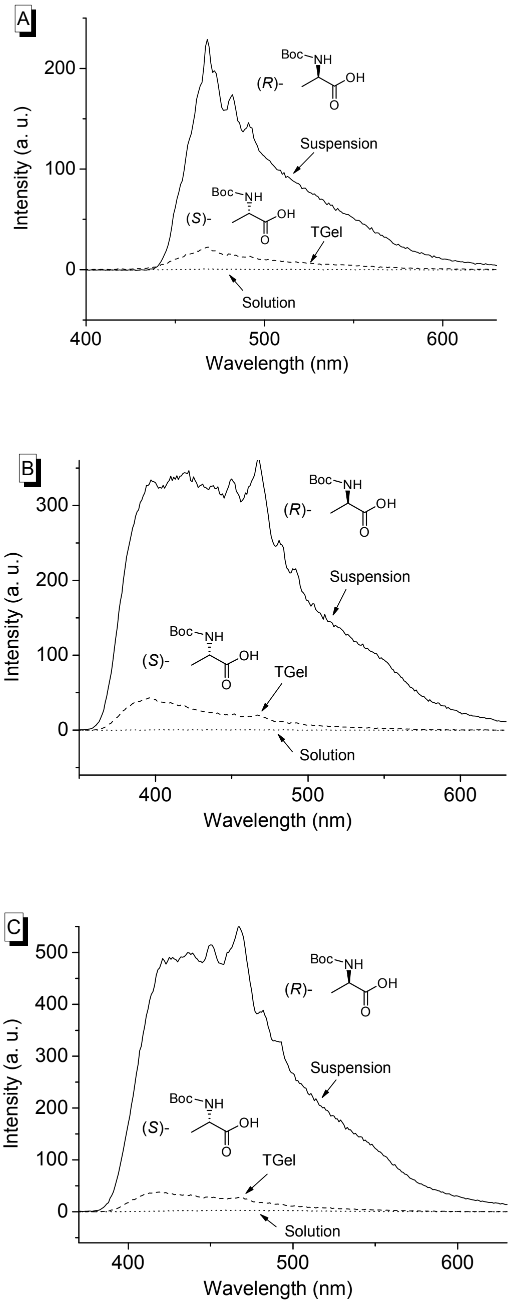

Figure S19. The fluorescence spectra of **1b** (A), **2a** (B) and **2b** (C) in the mixture of (*1S,2R*)-**3** and enantiomer of **6**. Solid line, that in suspension from mixture of (*1S,2R*)-**3** and (*R*)-**6**; dash line, that in TGel from mixture of (*1S,2R*)-**3** and (*S*)-**6**; dot line, that in solution obtained by heating TGel. [(*1S,2R*)-**3**] = [**6**] = 5[**1b**] = 5[**2**] = 10 mM in 1,2-dichloroethane.

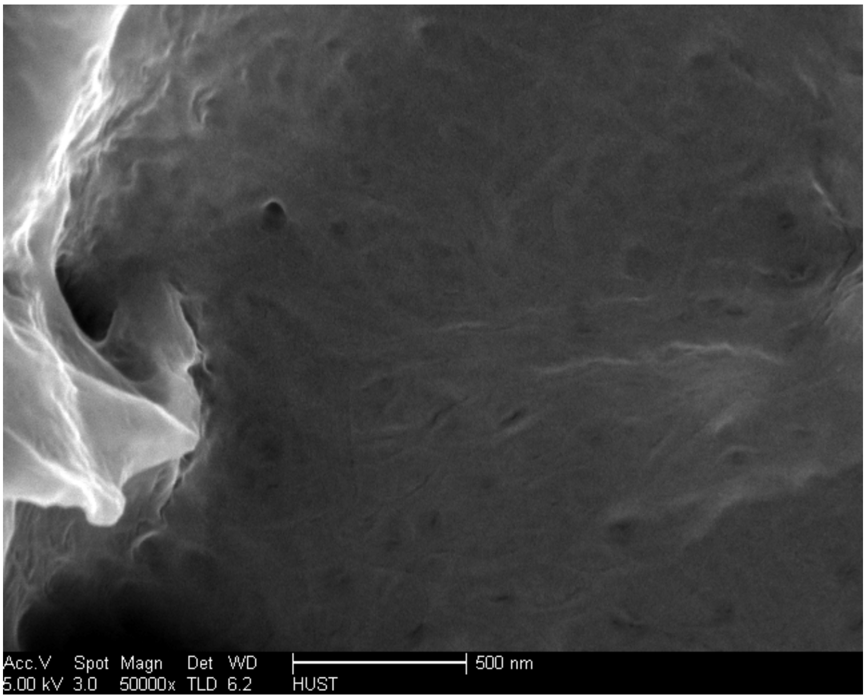

Figure S20. FE-SEM image of TGel formed by mixture of (*1S,2R*)-**3** and (*S*)-**6** in 1,2-dichloroethane.

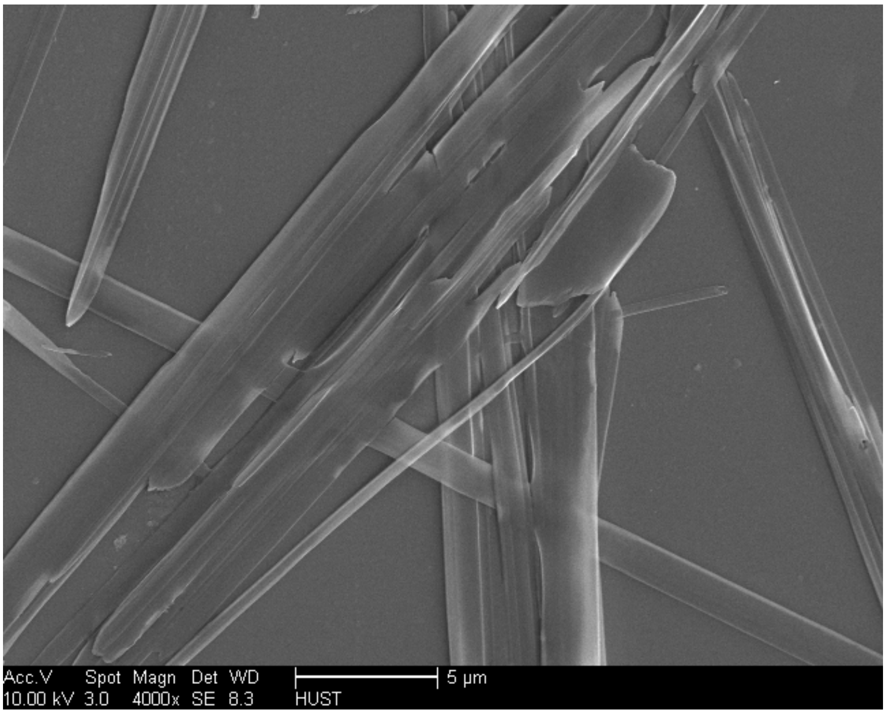

Figure S21. FE-SEM image of suspension formed by mixture of (*1S,2R*)-**3** and (*R*)-**6** in 1,2-dichloroethane.