Synthesis and optical properties of [C_{60}/C_{70}] fullerene derivatives containing spirobifluorene and imidazole units

CAIHUA LI[a*], HEPING ZENG[a], XINHUA OUYANG[a,b], RUIXIANG WANG[a], , WEI JI[b]

[a]*Institute of Functional Molecules, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510641, P. R. China*
[b]*Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore, 117542, Republic of Singapore*

A series of [C_{60}/C_{70}] fullerene derivatives containing different spirobifluorene and triphenyl imidazole were synthesized and confirmed by IR, ^{1}H NMR, ^{13}C NMR, MALDI-TOF-MS. Their optical limiting properties were investigated by nanosecond and femtosecond laser systems. Results showed that fullerene derivatives exhibited high optical limiting properties. Lower OL thresholds of 13.7, 14.9, 15.3, 23.3, and 24.0 J/cm^2 were observed for C_{70}-SBF, C_{60}-TPI, C_{60}-SBF, C_{60}-FSBF, and C_{60}-BTPI respectively with the linear transmittance of 75%, which implied that these optical limiting properties increased with the degree of conjugation and electron-donating or electron-accepting abilities of donors or acceptors in donor-acceptor (D-A) structures. The strong D and A with large conjugation is an effective way to enhance OL properties.

1. Introduction

Optical limiting (OL) materials, that exhibit high transmittance of low-intensity light and attenuate intense optical beams, have been studied extensively due to their application for laser protection [1-2]. However, most of the previous studies focused on nano- and pico-seconds due to the limited laser resources [3-4], while these studies offered excellent finding. The OL materials indicating good performance are still rare, especially in femtosecond timescale. Therefore, it will be essential to design and synthesize molecules with excellent OL performance.

[C_{60}/C_{70}]Fullerenes and their derivatives with large electron delocalization have been demonstrated for optical limiter during the past several years. In 1992, Tutt and Kost [5] found, for the first time, that C_{60} in toluene indicated excellent OL properties by nanosecond pulsed laser at a wavelength of 532 nm. Since then, many research groups [6-8] devoted themselves to study OL properties of [C_{60}/C_{70}]fullerene and their derivatives owing to their unique photophysical properties. It has been found that, [C_{60}/C_{70}]fullerenes derivatives with different substituents, such as methanofullerenes [9] and polycarbonate fullerenation [10], can enhance their OL

abilities significantly. Meanwhile, fluorene and imidazole derivatives with relatively unique delocalized π-bonds have also been extensively studied for a number of applications, especially in nonlinear optics [11-12]. In view of this regard, C_{60}-SBF and C_{60}-TPI were designed and synthesized by 1,3-dipolar cycloaddition containing spirobifluorene and triphenylimidazole units, expecting to gain excellent OL properties, we also synthesized other [C_{60}/C_{70}]fullerene derivatives, namely C_{70}-SBF, C_{60}-FSBF, C_{60}-BTPI and C_{60}-BBNPI, respectively. Their structures were shown in Scheme 1. The nanosecond and femtosecond laser OL are investigated at 532-nm and 780-nm wavelength. By analyzing OL characterizations, we confirmed that the OL property is enhanced by increasing the degree of molecular π-conjunction and electron – donating ability of donors or electron – accepting ability of acceptors in donor-acceptor (D-A) structures. Our findings offer a new avenue to design novel organic molecules exhibiting highly OL property, which are important systems for the study of fundamental properties as well as for use in nonlinear-optical application
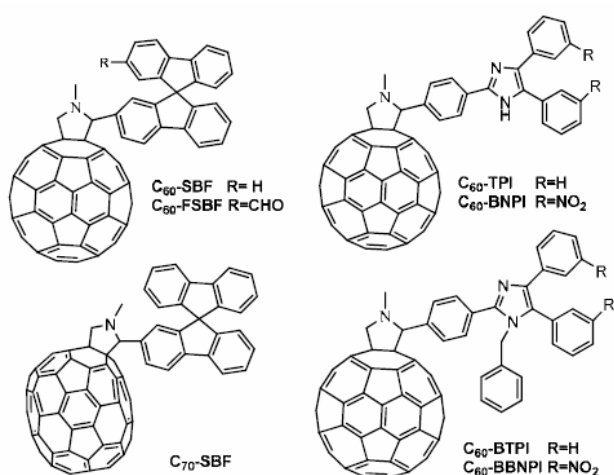
Scheme 1. Molecular structures of C_{70} and C_{60} derivatives
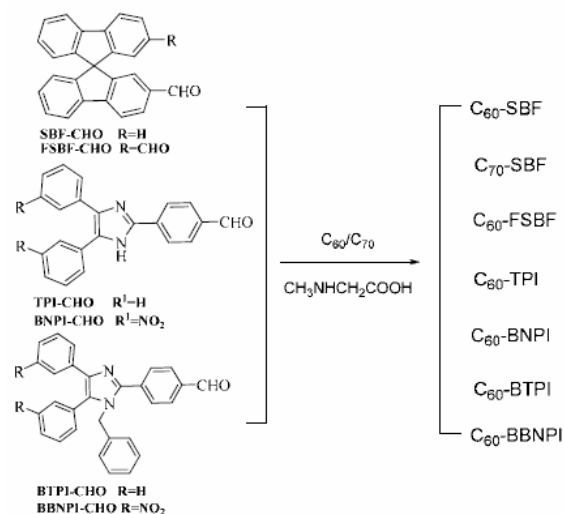
Scheme 2. Synthetic route of C_{70} and C_{60} derivates.

2. Experimental section

2.1. General

C_{60} and C_{70} (purity >99.9%) were purchased from 3D Carbon Cluster Material Co. of Wuhan University in China, other starting materials and solvents were purchased from Tokyo Casei Inc. 2-iodo-biphenyl was obtained according to reported literature.[13] All organic solvents were dried and distilled by appropriate methods. Column chromatography was carried out on silica gel (Wako C-300).

FT-IR spectra were recorded on a Perkin-Elmer Fourier transform infrared spectrometer using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were performed on BRUKER DRX-400 with $CDCl_3$ or $CDCl_3/CS_2$ as solvents. Chemical shifts (*d*) were given relative to tetramethylsilane (TMS). The coupling constants (*J*) were reported in Hz. The mass spectra were obtained on a Biflex-III MALDI-TOF and Esquire HCT PLUS. UV/Vis absorption and fluorescence spectra were recorded on HITACHI U3010 and Hitachi F-2500 fluorescence spectrophotometers.

The OL properties were measured in 1cm cell by nanosecond and femtosecond laser system using toluene as solvent (linear transmittance > 70%). Nanosecond laser was generated by Nd: YAG laser system with pulse wideness of 7 ns, 532 nm wavelength and 10 Hz frequency. Femtosecond laser was from Ti : Sapphire laser system with pulse wideness of 450 fs, 780 nm wavelength and 1 KHz frequency.

9, 9'-spirobifluorene and imidazole derivatives were obtained as described in the literatures [14-16]. Then, the fullerene derivatives were synthesized by 1, 3-dipolar cycloaddition reaction as shown in Scheme 2.

2.3. SBF-CHO[15-16]. In a vacuum glove box, $TiCl_4$ (2 mL, 18 mmol) was added to a solution of 3.0 g (9.5 mmol) 9, 9'-spirobi[fluorene] in distilled CH_2Cl_2 (80 mL) at 0 ^{o}C and sufficiently stirred for half an hour. Then, the dilution of 1.31g CH_3OCHCl_2 (11.4 mmol) in 10 mL CH_2Cl_2 were added by dropping funnel over 0.5 h at 0 ^{o}C. The temperature was allowed to reach R.T. and the mixture was stirred for an additional 12 h. 100 g of water with crushed ice were added to the reaction mixture and stirred for an additional 1 hour. The organic layer was separated and the aqueous layer was extracted three times with 20mL of CH_2Cl_2. The combined organic fractions were washed consecutively with saturated sodium bicarbonate (50mL), water (50mL), brine (50mL), dried over anhydrous sodium sulphate , and the solvent was evaporated. The residue was purified by chromatography on silica gel (dichloromethane / petroleum 1/6 as eluent) yielding 2.65 g of SBF-CHO as a light yellow foam. Yield: 81.2 % (2.65 g). m. p.: 210-211 ^{o}C; FT-IR (KBr): ν_{max}/cm^{-1}: 1738; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ(ppm): 9.82 (s, 1H), 7.99 (d, 1H, J=8 Hz) , 7.91-7.94 (m, 2H), 7.88 (d, 2H, J=7.6 Hz) , 7.44-7.38 (m, 3H), 7.26(s, 1H), 7.21 (t, 1H, J= 7.6 Hz), 7.12 (t, 2H, J= 7.6 Hz), 6.80(d, 1H, J=7.6 Hz), 6.71(d, 2H, J=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 191.7, 150.1, 149.7, 147.9, 147.5, 141.9, 140.2, 136.0, 130.3, 129.5, 128.1, 128.1, 128.0, 125.3, 124.4, 123.9, 121.2, 120.4, 120.25, 65.71; APCI- MS m/z(%): 344.9([M+1]$^+$, 100).

2.4. FSBF-CHO.[16]. The synthetic approach was similar to the synthesis of SBF-CHO, only changing the molar ratio of CH_3OCHCl_2 and 9,9'-spirobi[fluorene] to 2.5 : 1, which allowed to obtain the diformylation product, yield: 71.8 %. m.p. >300 ^{o}C; FT-IR (KBr): ν_{max}/cm^{-1}: 1690; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ (ppm): 9.78 (s, 2H), 7.96 (d, 2H J=8 Hz), 7.86-7.90 (m, 4H), 7.40 (t, 2H, J=7.6 Hz), 7.14-7.17 (m, 4H), 6.70 (d, 2H, J=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) :191.6, 148.9, 148.6, 148.0,

140.3, 136.1, 131.2, 129.7, 128.5, 124.6, 124.2, 121.5, 120.6, 65.5; APCI – MS m/z (%): 373.1([M+1]$^+$, 100).

2.5. 1, 2-bis(3-nitrophenyl)ethane-1,2-dione. Benzil (3 g, 14.3 mmol) was added to the mixed acid solution (17 mL) (HNO$_3$:H$_2$SO$_4$:H$_2$O =4:4:9). The reaction solution was refluxed at 140 ^{o}C for 4 h. After cooled to room temperature, yellow precipitated was filtered, washed with water, dried and recrystallized from alcohol. The rude product was purified by chromatography on silica gel (dichloromethane and petroleum as eluent). Yield: 44%. m.p.124~126 ^{o}C; FT-IR (KBr) v/cm^{-1}: 3090, 1676, 1611, 1530, 1350, 902; ^{1}H NMR (400 MHz, CDCl$_3$) δ(ppm): 8.87(s, 2H), 8.56(d, 2H, J=8.0 Hz), 8.39(d, 2H, J=7.6 Hz), 7.80(t, 2H, J=8.0 Hz); APCI-MS m/z(%): 299.7([M+1]$^+$, 100). Anal. Calcd for C$_{14}$H$_8$N$_2$O$_6$: C, 56.01; H, 2.69; N, 9.33; O, 31.98. Found: C, 56.12; H, 2.71; N, 9.29; O, 31.89.

2.6. TPI-CHO.[17] A mixture of terephthalaldehyde (1.37 g, 10.2 m mol), benzil (1.4 g, 6.8 mmol), ammonium acetate (5 g, 65 mmol), and [Hmim]HSO$_4$ (0.01 mmol) in acetic acid (50 mL) was refluxed for 4 h. After reaction completed, the mixture was poured into water (200 mL) and adjusted pH to ~7 with ammonia. The yellow precipitated was filtered, dried and purified by chromatography on silica gel (ethyl acetate and petroleum as eluent) to afford TPI-CHO (1.5 g yield: 55%). m.p.242~244 ^{o}C; FT-IR (KBr) v/cm^{-1}: 3050, 2843, 2741, 1696,1604, 1582, 1503, 1440, 1208, 1168, 1071, 765; ^{1}H NMR (400 MHz, CDCl$_3$) δ(ppm): 12.99 (s, 1H), 10.01 (s, 1H), 8.29 (d, 2H, J=8.0 Hz), 8.01(d, 2H, J=8.0 Hz), 7.54 (d, 4H, J=7.6 Hz), 7.38~7.34 (m, 6H); ESI-MS m/z(%): 325.3 (M$^+$, 100).

2.7. BNPI-CHO. The synthetic approach was similar to the process of TPI-CHO. A reaction of 1, 2-bis(3-nitrophenyl)ethane-1, 2-dione instead of benzil afforded BNPI-CHO. Yield: 65%. m.p. 290~292 ^{o}C; FTIR (KBr) v/cm^{-1}: 3272, 2926, 2855, 1743, 1604, 1570, 1515, 1210, 1168, 901, 810, 728; ^{1}H NMR (400MHz, DMSO-d_6) δ(ppm): 13.40 (s, 1H), 10.06 (s, 1H), 8.45 (s, 2H), 8.33 (d, 2H, J=8.4 Hz), 8.30 (s, 1H), 8.16 (s, 1H), 8.06 (d, 2H, J=8.4 Hz), 7.95 (s, 2H), 7.76 (s, 1H), 7.64 (s, 1H). ^{13}C NMR (100MHz, DMSO-d_6) δ(ppm): 192.7, 148.3, 145.8, 136.1, 135.0, 130.6, 130.4, 130.4, 126.1; APCI-MS m/z (%): 415.2 ([M+1]$^+$, 100). Anal. Calcd for C$_{22}$H$_{14}$N$_4$O$_5$: C 63.77, H 3.41, N 13.52, O 19.31; found: C 63.96, H 3.48, N 13.14, O 19.42.

2.8. BTPI-CHO. To a solution of TPI-CHO 0.40 g (1.4 mmol) in DMF (5 mL), was added anhydrous potassium carbonate (0.5 g, 3.6 mmol). The suspension liquid was stirred for 45 min at R.T. Then, dilution of 0.41g (2.4 mmol) benzyl bromide in 10 mL DMF was added by dropping funnel over 30 minutes at R.T. After stirred for 24 h at R.T, reaction mixture was poured into water (100 mL), adjusted pH to ~7 with acetic acid and then extracted with ethyl acetate. Solvents were removed under vacuum. The obtained crude product was purified by chromatography on silica gel (ethyl acetate and petroleum as eluent) to afford BTPI-CHO 0.37 g. Yield: 74%. m.p.

178~180 ^{o}C; FTIR (KBr) v/cm^{-1}: 3050, 3033, 2933, 2843, 1697, 1606, 1499, 1290, 777, 678; ^{1}H NMR (400 MHz, CDCl$_3$) δ(ppm): 10.03 (s, 1H), 7.89-7.85 (m, 4H), 7.57 (d, 2H, J=7.6 Hz), 7.38~7.32 (m, 3H), 7.26~7.17 (m, 8H), 6.83 (m, 2H), 5.16 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ(ppm): 191.7, 146.4, 138.9, 137.1, 136.5, 136.0, 134.1, 131.3, 131.0, 130.58, 129.9, 129.2, 128.9, 128.8, 128.2, 127.6, 126.8, 126.7, 125.8, 48.5; ESI-MS m/z (%): 415.2 ([M+1]$^+$, 100). Anal. Calcd for C$_{29}$H$_{22}$N$_2$O: C 84.03, H 5.35, N 6.76, O 3.86; found: C 84.38, H 5.62, N 6.61, O 3.89.

2.9. BBNPI- CHO. Synthetic approach was similar to the synthesis of compound BTPI-CHO. Employing BNPI-CHO instead of TPI-CHO allowed us to obtain BBNPI- CHO. Yield: 78%; m.p.184~186 ^{o}C; FT-IR(KBr) v/cm^{-1}: 3086, 3033, 2924, 2854, 1701, 1606, 1570, 1350, 804, 695; ^{1}H NMR (400 MHz, CDCl$_3$) δ(ppm): 10.07 (s, 1H), 8.38 (s, 1H), 8.28 (d, 1H, J=7.6Hz), 8.07~8.04 (m, 2H), 7.98 (d, 2H , J=8.0 Hz), 7.92 (d, 2H ,J=8.0 Hz), 7.80 (d, 1H, J=8.0 Hz), 7.58-7.51 (m, 2H), 7.40 (t, 1H, J=8.0 Hz), 7.26~7.25 (m, 3H), 6.82 (t, 2H, J=7.6 Hz), 5.20 (s, 2H); ^{13}C NMR (100MHz, CDCl$_3$) δ(ppm): 191.5, 148.5, 148.4, 148.1, 137.8, 136.9, 136.6, 136.0, 135.4, 135.3, 132.4, 131.5, 130.3, 130.1, 129.4, 129.4, 129.3, 129.1, 128.2, 125.7, 125.6, 124.3, 121.8, 121.6, 49.1; APCI-MS m/z (%): 505.2 ([M+1]$^+$, 100). Anal. Calcd for C$_{29}$H$_{20}$N$_4$O$_5$: C 69.04, H 4.00, N 11.11, O 15.86; found: C 69.32, H 3.88, N 11.14, O 15.66.

2.10. C$_{60}$-SBF. 216 mg (0.3 mmol) of C$_{60}$, 53.4 mg (0.6 mmol) of sarcosine, and 379 mg (1.2 m mol) of SBF-CHO were dissolved in 100 mL of dry toluene under nitrogen atmosphere. After refluxing for 2 h, the brown solution was concentrated and raw solid product was purified by flash column chromatography on silica gel (100-200 mesh) to give C$_{60}$-SBF (45.8 mg, yield: 14.0%). FT-IR (KBr): v$_{max}$/cm^{-1}: 2921.41, 1260.84, 802.99, 525.24; ^{1}H NMR (400 MHz; CS$_2$/CDCl$_3$; Me$_4$Si) δ(ppm): 7.88-7.78(m, 2H), 7.68(d, 4H, J=7.6 Hz), 7.21(t, 3H, J=7.6 Hz), 7.03(t, 3H, J=8.4 Hz), 6.96(t, 1H, J=8.4 Hz), 6.59-6.54(m, 2H), 4.75 (m, 2H), 4.11 (d, 1H, J= 9.6 Hz), 2.08 (s, 3H); ^{13}C NMR (100 MHz, CS$_2$/ CDCl$_3$) δ(ppm):156.0, 153.8, 153.2, 153.1, 149.0, 148.5, 148.1, 147.3, 147.3, 146.6, 146.4, 146.3, 146.1, , 145.9, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 145.1, 144.7, 144.3, 143.1, 142.9, 142.6, 142.5, 142.2, 142.1, 142.0, , 141.9, 141.7, 141.6, 141.2, 140.2, 140.1, 139.9, 139.2, 137.7, 136.8, 136.6, 136.5, 135.7, 130.2, 130.2, , 130.1, 130.0, , 129.9, 129.8, 129.1, 128.3, 127.8, 125.4, 124.8, 124.2, 120.2, 120.1, 83.2, 77.3, 70.0, 68.7, 65.8, 40.1; MALDI-TOF m/z (%): 1090.4 (M$^+$,100) Anal. Calcd for C$_{88}$H$_{23}$N: C, 96.60; H, 2.12; N, 1.28, Found: C, 96.48; H, 2.14; N, 1.38,

2.11. C$_{60}$-FSBF. The synthetic approach was similar to the synthesis of compound C$_{60}$-SBF. Employing FSBF-CHO instead of SBF-CHO allowed us to obtain the C$_{60}$-FSBF. Yield: 5.73 %; FTIR (KBr): v$_{max}$/cm^{-1}: 2923, 1644, 1466, 730, 525; ^{1}H NMR (400MHz, CS$_2$/CDCl$_3$; Me$_4$Si) δ(ppm): 9.71 (s, 1H), 7.86-7-65(m, 7H), 7.29-7.19(m, 3H), 7.01(t, 3H, J=7.6 Hz), 6.54(d, 1H, J=7.6 Hz), 4.73- 4.80(m, 2H),

4.12 (d,1H, *J*=9.6Hz), 2.72 (s, 3H); ^{13}CNMR (100 MHz, CS$_2$/CDCl$_3$) δ(ppm): 189.7, 155.9, 153.7, 152.9, 149.8, 149.5, 149.1, 149.0, 148.8, 147.6, 147.3, 146.5, 146.4, 146.3, 146.2, 146.1, 145.9, 145.6, 145.4, 145.3, 145.2, 144.7, 144.6, 144.4, 144.3, 143.1, 143.0, 142.7, 142.6, 142.3, 142.1, 142.0, 141.9, 141.7, 141.6, 141.4, 141.2, 140.2, 140.1, 140.0, 139.2, 139.1, 137.1, 136.7, 136.6, 136.5, 136.3, 136.2, 135.8, 135.7, 130.6, 130.3, 129.9, 129.6, 129.1, 128.8, 128.3, 128.1, 127.1, 125.5, 125.2, 125.0, 124.6, 124.4, 124.1, 123.8, 123.4, 121.4, 121.1, 120.5, 83.2, 80.9, 70.0, 68.7, 65.6, 40.1; MALDI-TOF m/z (%): 1119.4 (M$^+$,100) Anal. Calcd for C$_{89}$H$_{23}$NO: C, 95.26; H, 2.07; N, 1.25; O, 1.43, Found: 95.39; H, 2.09; N, 1.14; O, 1.39.

2.12. C$_{60}$-TPI. The synthetic approach was similar to the synthesis of compound C$_{60}$-SBF. Using TPI-CHO instead of SBF-CHO allowed us to obtain the C$_{60}$-TPI. Yield: 8.0 %; FTIR (KBr) ν/cm^{-1}: 3376, 2917, 2772, 1571, 1511, 1477, 1426, 1370, 1332, 1260, 1180, 901, 832, 713, 526; ^{1}H NMR (400MHz, CS$_2$/ CDCl$_3$) δ(ppm): 7.73 (s, 3H), 7.48 (d, 4H, *J*=8.0 Hz), 7.29-7.46 (m, 5H), 7.10 (s, 1H), 6.99 (d, 2H, *J*=6.8 Hz), 4.78 (s, 1H), 4.72 (d, 1H, *J*=8.4 Hz), 2.60 (s, 3H) , 3.85 (d, 1H, *J*=6.4 Hz); ^{13}C NMR (100MHz, CDCl$_3$+CS$_2$) δ(ppm): 152.8, 151.3, 148.8, 147.3, 146.6, 146.4, 146.3, 146.2, 145.9, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 144.7, 144.4, 143.2, 143.1, 143.0, 142.7, 142.6, 142.5, 142.4, 142.2, 142.1, 142.0, 141.9, 141.7, 141.6, 141.5, 140.2, 139.9, 139.7, 139.6, 137.0, 136.8, 136.5, 135.9, 135.6, 134.9, 134.4, 133.5, 130.9, 130.3, 130.1, 129.4, 129.2, 129.1, 129.0, 128.6, 128.2, 127.9, 126.7, 83.2, 71.7, 70.1, 68.8, 40.0; MALDI-TOF-MS m/z (%): 1071.3 (M$^+$, 100). Anal. Calcd for C$_{84}$H$_{21}$N$_3$: C 94.11, H 1.97, N 3.92; found: C 94.45, H 1.89, N 3.65.

2.13. C$_{60}$-BNPI. The synthetic approach was similar to the synthesis of compound C$_{60}$-SBF. Employing BNPI-CHO instead of SBF-CHO allowed us to obtain the C$_{60}$-BNPI. Yield: 26%; FTIR (KBr) ν/cm^{-1}: 3026, 2923, 2853, 1604, 1526, 1493, 1346, 699, 553, 526; MALDI-TOF-MS m/z (%): 1160.5 (M$^+$, 100). Anal. Calcd for C$_{84}$H$_{19}$N$_5$O$_4$: C 86.82, H 1.65, N 6.03, O 5.51; found: C 86.94, H 1.76, N 5.95, O 5.35.

2.14. C$_{60}$-BTPI. The synthetic approach was similar to the synthesis of compound C$_{60}$-SBF. Employing BTPI-CHO instead of SBF-CHO allowed us to obtain the C$_{60}$-BTPI. Yield: 30%; FTIR (KBr) ν/cm^{-1}: 3061, 2947, 2778, 1602, 1498, 1482, 1450, 1332, 1179, 1120, 766, 697, 553, 527; ^{1}H NMR (400MHz, CS$_2$/CDCl$_3$) δ(ppm): 7.67 (d, 2H, *J*=8.0 Hz), 7.44 (d, 2H, *J*=7.2 Hz), 7.32-7.25 (m, 4H), 7.16 (d, 2H, *J*=6.8 Hz), 7.12-7.05 (m, 6H), 5.04 (s, 2H), 4.97-4.93 (m, 2H), 4.25 (d, 1H, *J*=9.6 Hz), 2.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$/CS$_2$) δ(ppm): 155.8, 153.6, 152.9, 152.7, 147.0, 146.9, 146.4, 146.2, 146.1, 146.0, 145.9, 145.8, 145.7, 145.5, 145.3, 145.1, 145.0, 144.9, 144.5, 144.4, 144.1, 142.9, 142.8, 142.5, 142.4, 142.3, 142.0, 141.9, 141.8, 141.7, 141.6, 141.5, 141.3, 140.0, 139.7, 139.5, 139.3, 138.2, 137.4, 137.1, 136.7, 136.3, 135.7, 135.5, 134.1, 134.0, 130.9, 130.8, 130.7, 129.9,

129.3, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.0, 127.8, 127.3, 126.7, 126.2, 125.7, 83.0, 82.6, 69.8, 68.8, 48.0, 39.8; MALDI-TOF-MS m/z(%): 1160.5 (M$^+$, 100). Anal. Calcd for C$_{91}$H$_{27}$N$_3$: C 94.04, H 2.34, N 3.62; found: C 94.25, H 2.29, N 3.46.

2.15. C$_{60}$-BBNPI. The synthetic approach was similar to the synthesis of compound (C$_{60}$-SBF). Employing BBNPI-CHO instead of SBF-CHO allowed us to obtain the C$_{60}$-BBNPI. Yield: 27%; FT-IR(KBr) ν/cm^{-1}: 3059, 2924, 2853, 2777, 1613, 1525, 1345, 1281, 738, 694, 573, 552, 525; ^{1}H NMR (400MHz, CDCl$_3$/CS$_2$) δ(ppm): 8.25 (s, 1H), 8.21 (d, 1H, *J*=7.6Hz), 7.98 (s,1H), 7.94 (d, 1H, *J*=8.0Hz), 7.84 (s,1H), 7.75 (t, *J*=8.8Hz,3H), 7.52-7.45 (m,2H), 7.34-7.30 (m,1H), 7.18-7.16 (m,3H), 7.07 (d, 1H , *J*=7.6Hz), 6.73 (s,2H), 5.01 (s,2H), 4.98-4.96 (m,2H), 4.27 (d, 1H, *J*=9.6Hz), 2.81 (s,3H); ^{13}C NMR (100MHz, CS$_2$/CDCl$_3$) δ(ppm): 155.9, 153.7, 152.9, 152.7, 148.8, 148.4, 148.3, 147.2, 146.5, 146.3, 146.2, 146.1, 145.9, 145.8, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 145.1, 144.7, 144.5, 144.4, 144.3, 143.1, 143.0, 142.7, 142.6, 142.5, 142.2, 142.1, 142.0, 141.9, 141.8, 141.7, 141.5, 140.2, 139.9, 139.4, 138.7, 137.3, 136.9, 136.7, 136.4, 136.3, 136.0, 135.7, 135.5, 132.1, 131.8, 130.0, 129.8, 129.2, 129.1, 129.0, 128.5, 128.3, 128.2, 128.1, 125.8, 125.6, 125.5, 125.3, 123.9, 121.5, 83.1, 77.0, 67.0, 69.0, 48.8, 40.01；MALDI-TOF-MS m/z(%):1250.5 (M$^+$). Anal. Calcd for C$_{91}$H$_{25}$N$_5$O$_4$: C 87.28, H 2.01, N 5.59, O 5.11; found: C 87.37, H 1.96, N 5.65, O 5.02.

2.16. C$_{70}$-SBF. The synthetic approach was similar to the synthesis of compound C$_{60}$-SBF. Employing chlorobenzene as solvent allowed us to obtain the C$_{70}$-SBF (60.8 mg, yield: 16.70%). FT-IR (KBr): ν$_{max}$/cm^{-1}: 2923, 2853 1645, 1507, 1419, 724, 527; ^{1}H NMR (400 MHz; CS$_2$/CDCl$_3$; Me$_4$Si) δ(ppm): 7.71-7.61(m, 4H), 7.35-7.29(m, 2H), 7.24-7.20(m, 2H), 7.15(t, 1H, J=8 Hz), 7.07-7.01(m, 2H), 6.96(t, 1H, J=8 Hz), 6.56-6.61(m, 2H), 4.02-3.88 (m, 2H), 3.37 (d, 1H, *J*=9.2Hz),2.30, 2.12, 2.11(major isomer)(s, 3H); ^{13}C NMR (100 MHz, CS$_2$/CDCl$_3$) δ(ppm): 158.8, 156.4, 154.8, 154.6, 151.9, 151.7, 151.3, 151.2, 151.0, 150.7, 150.6, 150.5, 150.4, 150.2, 149.9, 149.8, 149.3, 149.2, 149.1, 149.0, 148.9, 148.9, 148.8, 148.6, 148.3, 148.1, 147.8, 147.4, 147.1, 147.0, 146.9, 146.2, 146.1, 145.8, 145.7, 145.3, 144.5, 143.5, 143.4, 143.2, 143.1, 142.8, 142.7, 141.9, 141.6, 141.3, 141.0, 140.7, 140.1, 137.6, 137.4, 136.8, 136.4, 133.8, 133.5, 132.8, 132.3, 132.0, 131.6, 131.4, 131.3, 131.2, 129.1, 128.3, 128.2, 128.1, 127.8, 125.4, 124.7, 124.3, 124.2, 124.1, 123.8, 120.3, 120.3, 120.2, 120.7, 70.2, 68.8, 66.3, 61.8, 60.1, 43.6; MALDI-TOF: 1210.4 (M$^+$) Calcd for C$_{98}$H$_{23}$N: C, 96.94; H, 1.91; N, 1.15, Found: C, 96.81; H, 1.95; N, 1.24

3. Results and discussion

The pathway to fullerene substitution as shown in Scheme 2 was generated by [6,6] cycloaddition to C$_{60}$ or C$_{70}$, to yield the desired fulleropyrrolidine. It was clearly confirmed by MALDI-TOF-MS that all the fullerene

derivatives were monoadducts. Unlike to all the C$_{60}$ derivatives, C$_{70}$-SBF was testified to be a mixture of three isomeric monoadducts by three distinct *N*-methyl resonances presented from δ 2.30 to δ 2.11 ppm in 1H NMR spectrum. They were resulted from the addition to six, 6-ring fusions of C$_{70}$ at the 1, 9-; 7, 8-; and 22, 23-bonds, as previously reported for the cycloaddition of *N*-methyl-azomethine ylide to C$_{70}$ derivatives.[18]

The absorption spectra of the C$_{60}$ derivatives in toluene were plotted in Figure 1a. It can be found all of them exhibit a sharp absorption band at ~433 nm, which is the characteristic peak of [6,6] bridged monoadducts[19] and a weak band at approximately 705 nm due to the singlet excited states absorption. [20] As shown in the absorption spectra of C$_{60}$-SBF and C$_{60}$-FSBF, no profile change was observed, suggesting no appreciable interaction in the ground state between the C$_{60}$ and SBF or FSBF moieties [21]. The same results were obtained for C$_{60}$-TPI, C$_{60}$-BNPI, C$_{60}$-BTPI and C$_{60}$-BBNPI.
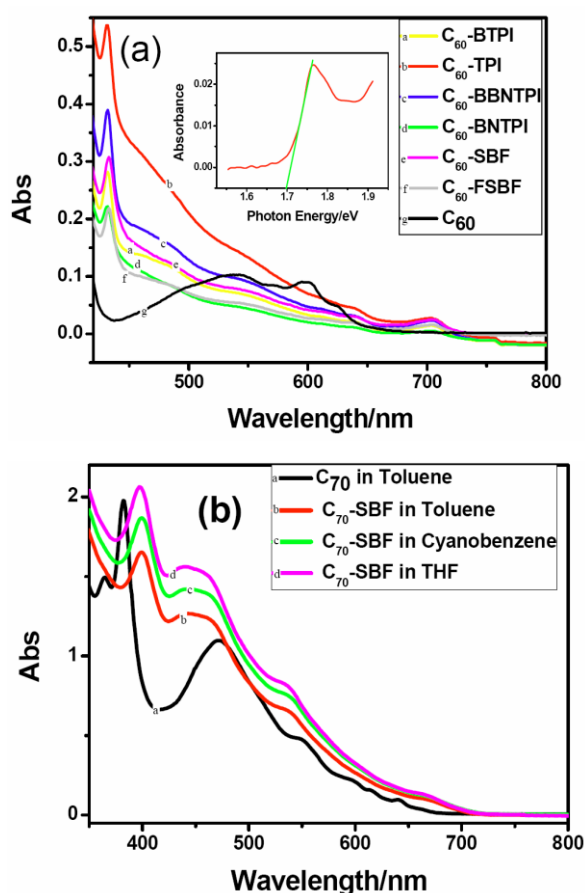
Fig. 1 Ground state absorption spectra of C$_{60}$-FSBF, C$_{60}$-SBF, C$_{60}$-TPI, C$_{60}$-BTPI, C$_{70}$-SBF, and C$_{60}$-BBNPI in the different solvents.

Fig. 1b shows absorption spectra of C$_{70}$-SBF in three different solvents and pristine C$_{70}$ in toluene. In the figure, C$_{70}$ spectral is remarkably different from C$_{70}$-SBF. However, the C$_{70}$-SBF absorbance peaks in the three solvents are nearly overlapping, it can be concluded

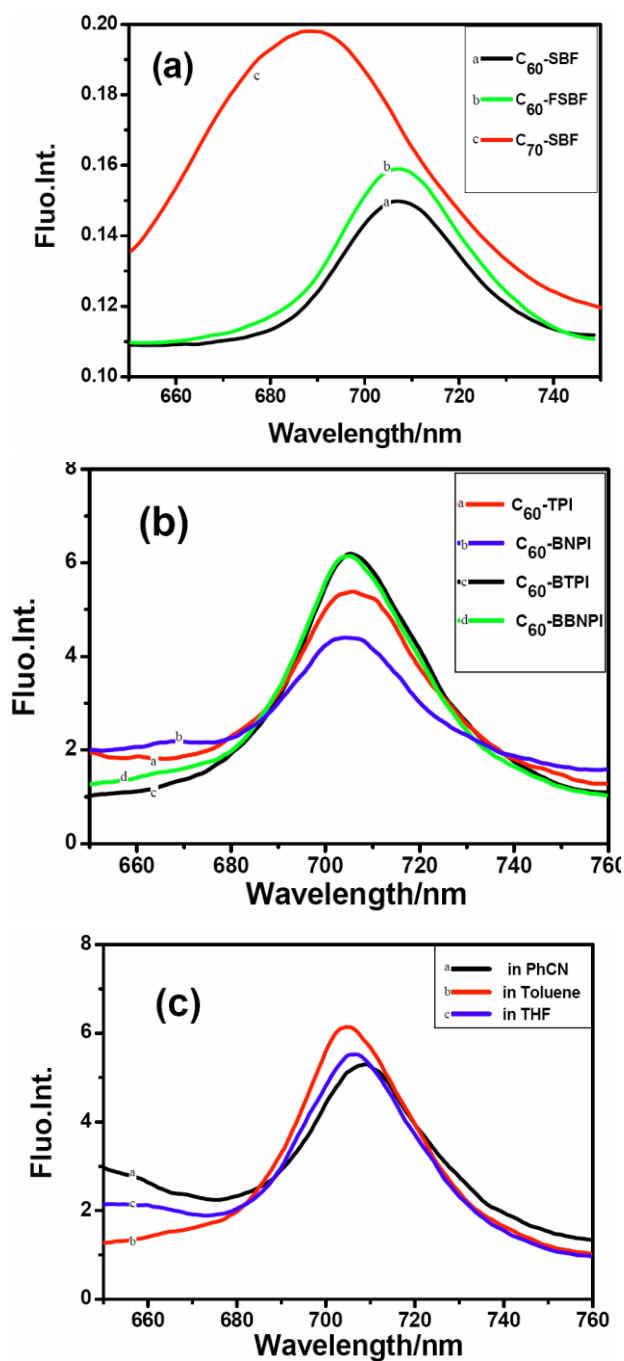C$_{70}$-SBF doesn't show solvent effect. Similar results were also observed among others C$_{60}$ derivatives.

Fig. 2. Fluorescence spectra of C$_{60}$-FSBF, C$_{60}$-SBF, C$_{60}$-TPI, C$_{60}$-BTPI, C$_{70}$-SBF, and C$_{60}$-BBNPI

(λex =400 nm) in the different solvents.

As shown in Fig. 2, all derivatives exhibit one main peak at approximately 719 nm (C$_{60}$ derivative) and 690 nm (C$_{70}$-SBF) in toluene, which are attributed to fullerene emission, corresponding to the fullerene excited singlet state emission [22–24]. By comparing fluorescence peak (719nm) with absorption peak (705nm), it was revealed that C$_{60}$ derivatives showed a small Stokes shift. As shown

in Fig. 3a, the intensity of C_{60}-FSBF was higher than that of C_{60}-SBF with the same concentration (1×10^{-4} mol/L) by introduction of fluorophore aldehyde group. In addition fluorescent intensities of C_{60}-BTPI and C_{60}-BBNPI were enhanced significantly due to the fluorochrome benzyl. On the contrary, strong electrophilic nitro group quenched the fluorescence in C_{60}-BNPI. So fluorescence intensity of C_{60}-TPI was higher than that of C_{60}-BNPI.

The fluorescent spectra of C_{60}-BBNPI in different solvents were shown in Figure 2c. With large polarities solvent (THF andbenzonitrile), the maximal peaks shift to red significantly compared with theirs in non-polar toluene, accompanied by decreasing luminescence intensity. Similar tendencies were observed in the others C_{60}/C_{70} derivatives. The red-shift phenomena may be due to the stabilization of excited singlet state (π-π*) in polar solvent, which is more intensive than that of ground state. Meanwhile, fluorescence is quenched in polar solvent induced by deactivation of excited singlet state via intersystem crossing process.

To compare the OL effect, concentrations of these derivatives were adjusted to same linear transmittance of 75% for nanosecond laser and 82.5% for femtosecond laser.

The normalized transmittances of these derivatives as a function of the incident irradiance are shown in Fig. 3. As displayed in Fig. 3a, The transmittance begin to deviate from the linear transmission when the incident irradiance is increased beyond ~7 GW/cm^2 (except C_{60}-BBNPI, 45 GW/cm^2), a typical OL was manifested with the light transmittance reduced down to 59.7, 65.2, 66.0, 69.0 69.1, and 73.2 at ~100 GW/cm^2, respectively, for the dyads C_{60}-FSBF, C_{60}-SBF, C_{60}-TPI, C_{60}-BTPI, C_{70}-SBF, C_{60}-BBNPI. Figure 4b showed normalized transmittances in nanosecond timescale. With increasing incident intensity, the transmittances of these derivatives clearly decrease. The thresholds of these derivatives are at the region of 10-20 J/cm^2. Table 1 listed the optical-limiting onsets and thresholds of these derivatives, which are important parameters in characterizing the merit of these optical limiters.

As shown in Fig. 3 and Table 1, the derivatives in nanosecond laser pulse exhibit better OL properties than theirs in femtosecond laser. To interpret the notable difference between the ns and fs results, we should use energy levels in these derivatives. In nanosecond timescale, the OL phenomena in these derivatives were from nonlinear absorption containing S_0-S_1, S_1-S_n, T_1-T_n and intersystem crossing (ISC) absorption, which have been demonstrated by many groups.[25-26]However, in femtosecond timescale, the OL phenomena in these molecules were from nonlinear absorption containing only S_0-S_1, S_1-S_n, Since the timescales of T_1-T_n and intersystem crossing (ISC) absorption are more than 100 ps, femtoscond laser cannot detect these processes. Furthermore, for nanosecond, the thermally induced scattering effects are significant to contribute their nonlinear OL.
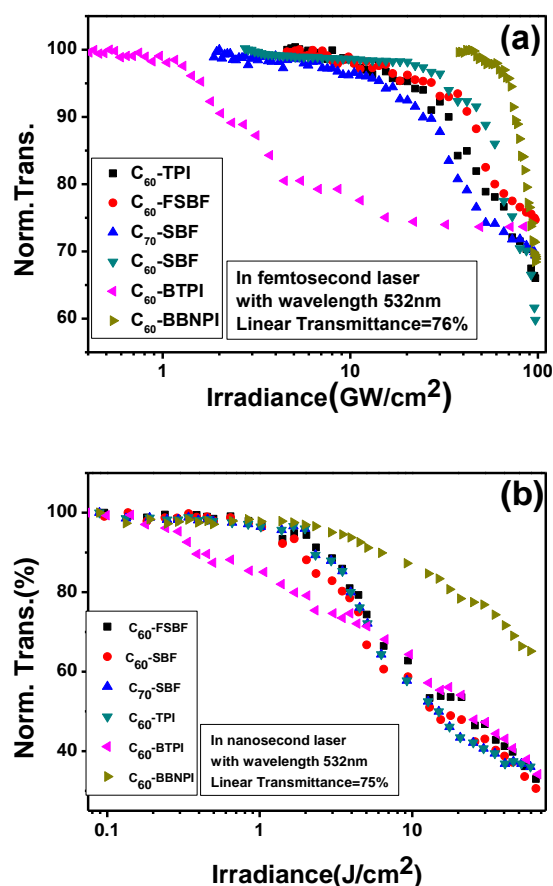

Fig..3　Normalized transmittances of C_{60}-FSBF, C_{60}-SBF, C_{60}-TPI, C_{60}-BTPI, C_{70}-SBF, and C_{60}-BBNPI in toluene.

Table1 OL Properties of the fulleropyrrolidine derivative.

	NS　laser		FS　laser	
	Onset [a] (J/cm^2)	Threshold[b] (J/cm^2)	Onset [a] (GW/cm^2)	Transmittance[c] (%)
C_{60}-SBF	0.088	15.3	5.07	65.2
C_{60}-FSBF	0.24	23.3	7.12	66.0
C_{60}-TPI	0.086	14.9	2.75	59.7
C_{60}-BTPI	0.143	24.0	0.51	73.2
C_{60}-BBNPI	0.089	/	45.2	69.1
C_{70}-SBF	0.136	13.7	1.98	69.0

[a] Irradiance which the light energy transmitted starts to deviate from Beer's law. [b] Defined as the incident fluence at which the solution transmittance falls to 50% of the linear transmittance. [c] The normalized transmittance when the irradiance is 100GW/cm^2.

Among these derivatives, the electron – donating abilities of donors play an important role in enhancing the OL properties. C_{60} and C_{70} are good electron acceptors [27]. SBF and imidazole derivatives are usually acted as electron donor. As shown in Fig.3 and Table 1, the OL

property is in the order of C$_{70}$-SBF > C$_{60}$-TPI > C$_{60}$-SBF > C$_{60}$-FSBF > C$_{60}$-BTPI > C$_{60}$-BBNPI. For C$_{60}$-BTPI and C$_{60}$-BBNPI, the electron - donating ability of BBNPI is very poor owing to electron- withdrawing nitro groups, accordingly, the OL property of C$_{60}$-BBNPI has been weakened noticeably. Likewise, the formyl group in FSBF reduced its electron – donating ability, so the OL property of C$_{60}$-FSBF was inferior to that of C$_{60}$-SBF. As shown in Table 1, the gap of OL property between C$_{60}$-SBF and C$_{60}$-FSBF is smaller than that of C$_{60}$-BTPI and C$_{60}$-BBNPI. This may be attributed to substituted number and position. In spirobifluorene, two biphenyl moieties are orthogonally fused at the central carbon atom, the π-conjugates system cannot be formed in the molecule. Furthermore, formyl and C$_{60}$ in C$_{60}$-FSBF are located at different section of spirobifluorene, the formyl in C$_{60}$-FSBF will be little affected owing to its non-conjugated bond in spirobifluorene, comparing with the structure of C$_{60}$-BTPI and C$_{60}$-BBNPI.

The electronic acceptors also play an important role to enhance OL properties. Comparing the structure of C$_{70}$-SBF with C$_{60}$-SBF, it can be found they have the same donor and different acceptor. As shown in Table 2, the values of threshold are 13.7 and 15.3 J/cm^2, for C$_{70}$-SBF and C$_{60}$-SBF, respectively. It is clear that the OL property of C$_{70}$-SBF is superior to that of C$_{60}$-SBF, implying that the strong electron-accepting group of C$_{70}$ [18] can also enhance the performance in the molecules of the D-A system.
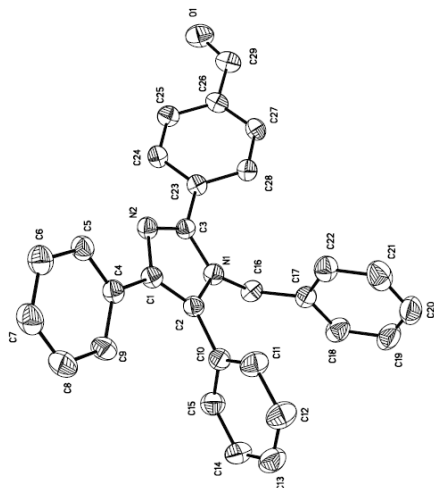

Fig..4 The crystal structure of BTPI-CHO

The results in Fig. 3 and Table 1 also reveal the significant effects of π-conjugates in enhancing OL properties. For C$_{60}$-TPI and C$_{60}$-BTPI, the threshold of them are 14.9 and 24.0 J/cm^2 in nanosecond timescale. Besides, in femtosecond timescale, their light transmittance reduced down to 59.7 and 73.2 respectively at ~100 GW/cm^2. This clearly indicates that C$_{60}$-TPI showed better performance than C$_{60}$-BTPI's. TPI in C$_{60}$-TPI could form large π-conjugates system, though the two phenyl rings at 4 and 5 positions were slightly

distorted due to steric hindrance. By contrast, the single crystal of BTPI-CHO was shown in Fig.4, the phenyl ring at 5 position was nearly perpendicular to the imidazol ring, the degree of π-conjugates in BTPI of C$_{60}$-BTPI decreased significantly. Therefore, the OL property of C$_{60}$-BTPI is weakened mainly due to the lower degree of π-conjugates.

4. Conclusions

We have demonstrated an approach toward the design and synthesis of [C$_{60}$/C$_{70}$]fullerene derivatives with high OL properties. Lower OL thresholds of 13.7, 14.9, 15.3, 23.3, and 24.0 J/cm^2 were observed for C$_{70}$-SBF, C$_{60}$-TPI, C$_{60}$-SBF, C$_{60}$-FSBF, and C$_{60}$-BTPI respectively with the linear transmittance of 75%. In addition, the OL properties in femtosecond timescale were found to be inferior to theirs in nanosecond timescale, which was due to lack of thermally induced scattering effects and triplet excited states absorption. The strong D and A with large conjugation is an effective way to enhance OL properties. Our findings open a new avenue for designing molecules with high OL properties.

Supplementary material.

Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Centre with CCDC reference number for complex CCDC 739567.

References

[1] G.. J. Mains, J.M. White, J. Phys. Chem. **95,** 112(1991).
[2] D. J. Clarke, J. G. Matisons, G. R. Simon, M. Samoc, A. Samoc, Appl. Organometal. Chem. **22**, 460(2008).
[3] L. Polavarapu, N. Venkatram, W. Ji, QH. Xu, *ACS* Applied Materials & Interfaces, **1**, 2298 (2009).
[4] Q.-F. Zhang, Y.-N. Xiong, T.-S. Lai, W. Ji, X.-Q. Xin, J. Phys. Chem. B, **104,** 3446(**2000)**.
[5] L.W. Tutt and A. Kost, Nature **356**, 225(1992).
[6] G.. Mountrichas, S. Pispas, E. Xenogiannopoulou, P. Aloukos, S. Couris, J. Phys. Chem. B **111**, 4315(2007).
[7] W. Ji, H.- I. Elim, J. He, F. Fitrilawati, C. Baskar, S. Valiyaveettil, W. Knoll, J. Phys. Chem. B **107**, 11043 (2003).

[8] J.E. Riggs, Y.P. Sun, J. Phys. Chem. A **103**, 485 (1999).

[9] D. Felder, D. Guillon, R. Levy, A. Mathis, J.F. Nicoud, J.F Nierengarten, J.L Rehspringer, J. Schell, J. Mater. Chem. **10**, 887 (2000).

[10] B.Z. Tang, H. Peng, S.M. Leung, C.F. Au, W.H. Poon, H. Chen, X. Wu, M.W. Fok, N.T. Yu, H. Hiraoka, C. Song, J. Fu, W. Ge, G.K.L. Wong, T. Monde, F. Nemoto, K.C. Su, Macromolecules **31**, 103(1998).

[11] H. Peng, J.W.Y. Lam, B.Z. Tang, Macromol. Rapid Commun. **26**, 673(2005).

[12] B. Kevin D, B. Mykhailo V, H. Florencio E, P. Olga V, J. Phys. Chem.C. **112**, 5618(2008).

[13] R .Wu, J. S. Schumm, D. L. Pearson, et al.. J. Org. Chem. **61,** 6906(1996).

[14] R.G. Clarkson, M. Gomberg, J.Am.Chem.Soc. **52**, 2881(1930).

[15] C. Poriel, Y. Ferrand, S. Juillard, L.M. Paul, G. Simonneaux, Tetrahedron. **60**, 145(2004).

[16] L. Mattiello, G. Fioravanti, , Synth.   Commun., **31**, 2645(2001).

[17] A. R. Khosropour, Can. J. Chem. **86**, 264(2008).

[18] X.H. Ouyang, H.P. Zeng, W. Ji, J. Phys. Chem. B. **113**, 14565(2009).

[19] F. Langa, P. de la Cruz, E. Espildora, A. Gonzalez-Cortes, A. de la Hoz, V.   Lopez-Arza, J. Org. Chem. **65**, 8675(2000).

[20] M. Meneghetti, R. Signorini, M. Zerbetto, R. Bozio, M. Maggini, G. Scorrano, M. Prato, G. Brusatin, E. Menegazzo, M. Guglielmi, Synth.Met. **86**(1-3), 2353(1997).

[21] H.P. Zeng, T. Wang, A.S.D. Sandanayaka, Y. Araki, O. Ito, J. Phys. Chem. A **109**, 4713(2005).

[22] S. Cattarin, P. Ceroni, D.M. Guldi, M. Maggini, E. Menna, F. Paolucci, S. Roffia, Gi. Scorrano, J. Mater. Chem. **9**, 2743 (1999).

[23] Y. Zhao, Y. Fang, Y. Jiang, Spectrochim. Acta A **64A**, 564(**2006)**.

[24] F. Sarah, B.S. Mario N, F. Aleksandre, B. Rene V, L. Sydney, G. Barbara,   Chem. Phys **263**(2-3), 437 (2001).

[25] S. Foley, M.N. Berberan-Santos, A. Fedorov, R.V. Bensasson, S. Leach, B. Gigante, Chem. Phys. **263**, 437(2001).

[26] R.L. Sutherland, M.C. Brant, J. Heinrichs, J.E. Rogers, J. E. Slagle, D.G. McLean, P.A. Fleitz, J. Opt. Soc. Am. B **22,** 1939(2005).

[27] P.W. Fowler, A. Ceulemans, J. Phys. Chem. **99**, 508(1995).

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*Corresponding author: caihua.li@mail.scut.edu.cn