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Energy level tunable pre-click functionalization of [60]fullerene for nonlinear optics

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ABSTRACT

[2+2] click chemistry followed by Prato reaction is reported the first time for energy level tunable functionalization of C₆₀. The novel kind of D–A–A C₆₀ charge-transfer complexes exhibits strikingly enhanced optoelectronic properties and significant third-order nonlinear optical potentials. Meanwhile, structures of the 'click' C₆₀ products were fully characterized by NMR, IR, and MS. By introducing TCNE, TCNQ, F₄-TCNQ click monomers, we obtained energy level tunable fullerene derivatives in high solubility, which was beneficial for processing. Furthermore, UV–vis spectra were enlarged with end-absorptions into the near infrared region, indicating excellent nonlinear optical properties. The electrochemical properties have been studied by cyclic voltammograms, which were in good correlation with the optical spectroscopic and DFT data.

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1. Introduction

Materials with large third-order optical nonlinearities and fast nonlinear optical (NLO) responses are considered to be promising candidates for photonic applications, such as optical communication, data processing, optical switching, and so forth.¹ The study of molecular materials for third-order nonlinear optics has focused primarily on organic compounds,² among which materials with high molecular hyperpolarizabilities (strongly dipolar conjugated π -systems) exhibit strong third-order nonlinearity.³ Especially, electron-deficient C₆₀ stands out in view of its unique threedimensional π -electron delocalization pattern.

However, the poor solubility, relatively large bandgap and low charge delocalization of pristine fullerenes severely limit their derivatization and utilization.⁴ To circumvent this hurdle, a variety of approaches⁵ have been developed. In particular, covalent functionalization is attracting wide interest as it can greatly alter the physical and chemical properties of fullerene through attachment of strong electron-withdrawing soluble moieties. Clearly, effective synthetic methodologies for the appending side chains are of great significance, in which high selective and productive click chemistry⁶ comes to the forefront.

As a highly efficient and catalyst-free reaction, the thermal [2+2] cycloaddition followed by retro-electrocyclization, between

click reagents and alkynes, i.e., '[2+2] click reaction'⁷ has gained enormous attention. Taking advantage of this reaction, we should be able to availably modulate energy levels and optimize electronic states via appropriate option of click reagents with different conjugation lengths. To the best of our knowledge, there is no report so far on the use of [2+2] click reaction to improve the solubility and optoelectronic properties of fullerenes. Therefore, the combination of the well-known Prato reaction⁸ and the above-mentioned highyielding click reaction is a powerful and novel strategy in the functionalization of C₆₀ (Scheme 1).



Scheme 1. General functionalization of fullerene via Prato reaction.

2. Results and discussion

2.1. Synthesis

The overall synthetic scheme was depicted in Fig. 1, and highlight was the novel type of monodonor–bisacceptors (D-A-A)





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Fig. 1. General scheme for the synthesis of click products C series (C1–C3) and further functionalized D–A–A type C₆₀ derivatives S series (S1–S3). The percentage in the brackets was productivity.

charge-transfer C₆₀ complexes (**S1–S3**). The synthesis of the D–A–A type C₆₀ derivatives involved a two-step procedure. First, the series of strong electron donors **C1–C3** was synthesized by the high-yielding [2+2] click reaction using ditetracyanoethene (TCNE), 7,7,8,8-tetracyanoquiodimethane (TCNQ), and 2,3,5,6-tetrafluoro-7,7,8,8-tetra cyanoquinodimethane (F₄-TCNQ) as click reagents. Then the electron donors were appended by reacting with fullerene and sarcosine in *o*-dichlorobenzene (*o*-DCB). The [2+2] click reactions had significantly high yields approximately 90%. The novel 'click' C₆₀ products **S1–S3** with tunable energy levels and different conjugation lengths exhibited high stability to moisture and air as well as enhanced solubility in common organic solvents, as compared to C₆₀. All the newly synthesized compounds were fully characterized by NMR, FTIR, UV–vis, mass and other spectroscopic methods.

2.2. UV-vis spectroscopy

The normalized UV-vis absorption spectra of the click compound **C2** and the corresponding C_{60} derivative **S2** were shown in Fig. 2a. The absorption peaks of C2 were located at 270, 305, 489, and 693 nm, respectively. Upon appending fullerene, these bands were shifted to 291, 320, 479, and 716 nm, respectively. The band at 291 nm was much higher in intensity due to the overlap of the fullerene absorption band.⁹ The 23 nm bathochromic shift of the end absorption peak was attributed to the electronic interactions between the click donor and C₆₀ acceptor moieties.¹⁰ As shown in Fig. 2b, all the prepared C₆₀ derivatives exhibited intense chargetransfer (CT) bands with end-absorptions under 1000 nm, indicating excellent nonlinear optical materials.¹¹ Compared with **S1** (477 nm), the red-shift in the maximum absorption was 241 and 365 nm for **S2** and **S3**, respectively. The extent of bathochromic shifts was dramatically facilitated by the elongation of conjugation lengths of molecular backbones and enhancement of electron affinities via introduction of strong electron-withdrawing substitutes,¹² from which an effective way to modulate the optic properties of C₆₀ derivatives was achieved.

2.3. Electrochemistry

The electronic structures of the 'click' C_{60} derivatives in the ground electronic state were visualized by density functional



Fig. 2. UV-vis absorption spectra of (a) C2 and S2; (b) S1-S3 in methylbenzene at 298 K. The inset photographs were the chemical structures.

theory (DFT) calculations.¹³ In Fig. 3, the optimized structures and electron densities of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the 'click' C_{60} derivatives were shown. From **S1** to **S3**, The LUMO energy was greatly decreased at the same time the HOMO was slightly



Fig. 3. Optimized structures and electron distributions of LUMO and HOMO of (1) **S1**; (2) **S2**; (3) **S3** calculated at the B3LYP/3-21G level.

increased. Consequently, the LUMO–HOMO gap was gradually lowered due to the increase of π -electron numbers and strain energy release of C_{60} carbon cage.¹⁴ The electron densities in the LUMO were all located on the C_{60} moiety, suggesting that C_{60} act as the acceptor. On the other hand, except for **S1**, the HOMOs were found on the click entities, indicating that the click moieties behave as the donor groups and suggesting the hole distribution in the charge-separated state. To confirm this computational prediction, electrochemical studies were performed to evaluate the redox potentials of the 'click' C_{60} derivatives.

The cyclic voltammograms and energy levels of the 'click' C_{60} derivatives were shown in Fig. 4(1). Compared with **S1**, the TCNQ and F4-TCNQ adducted click-fullerenes **S2** and **S3** showed anodically shifted onset oxidation potentials (E_{on}^{ox}) at 0.47 and 0.53 V, which was assigned to the more efficient interaction of the click donor moiety and C_{60} acceptor, making the oxidation more difficult.

On the other hand, **S2** and **S3** exhibited easier reductions (E_{on}^{red} at -0.64 and -0.54 V, respectively), probably caused by the expanded π -conjugation of the donor moieties and introduction of strong electron-withdrawing radicals, such as fluorine atoms in F4-TCNQ.¹⁵ Consequently, from **S1** to **S3**, the LUMO energy levels and electrochemical band gaps calculated from the onset oxidation and reduction potentials, were both on the monotone decreasing trend (Fig. 4(2)). Furthermore, these electrochemical band gaps were in good correlation with the optical spectroscopic and DFT data that they were reduced upon moving from **S1** to **S2** and on to **S3**, as summarized in Table 1.

2.4. Nonlinear optics

Z-scan experiments were utilized to verify the possibility of NLO enhancements via functionalization of C₆₀, with parameters summarized in Table 1. Furthermore, Fig. 5 displayed the nonlinear absorptive and refractive behavior of **S2** and a good fit between the experimental data and the theoretical curve was achieved. As shown in Fig. 5a, the absorption decreased with increasing intensity of the incident laser, with the light transmittance increasing to 115% at the focal point. Except for **S3** (Introduction of strong electron-withdrawing atom fluorine greatly impaired NLO properties, leading to no refractive data), the third-order nonlinear optical susceptibility ($\chi^{(3)}$) was in the order of C₆₀¹¹ < **S1** < **S2**, which could be ascribed to the structural symmetry violation¹⁷ and the elongation of conjugation length¹⁸ via functionalization. Therefore, this could be an efficient guidance for molecular design to improve NLO properties of fullerene.

3. Conclusions

In summary, a series of novel D–A–A type C_{60} derivatives was synthesized via a two-step procedure of [2+2] click chemistry followed by Prato reaction. Computational studies of DFT predicted the enlargement of conjugation lengths and electron-withdrawing abilities to decrease energy gaps, and both electrochemical and



Fig. 4. (1) Cycle voltammograms of 'click' C₆₀ derivatives S1–S3 in methylbenzene/Bu₄NPF₆ at 293 K; (2) LUMO and HOMO energy levels of C₆₀ (a: see Ref. 16) and S1–S3.

 Table 1

 Electrochemical and NLO properties of products S1–S3

Materials	$E_{\rm on}^{\rm oxa}\left({\sf V}\right)$	$E_{\rm on}^{\rm reda}\left({\sf V}\right)$	$E_{g}^{b}(eV)$	$E_{g}^{c}(eV)$	$E_{g}^{d}(eV)$	NLO properties		
						β (×10 ⁻¹² m/W)	$n_2 (\times 10^{-19} \text{ m}^2/\text{W})$	χ (3) (×10 ⁻¹³ esu)
S1	0.42	-0.83	1.25	1.87	2.55	-4.65	3.37	5.24
S2	0.47	-0.64	1.11	1.30	2.31	-7.75	4.76	8.83
S3	0.53	-0.54	1.07	1.06	1.60	-6.28	_	—



Fig. 5. Z-scan results of S2 in tetrahydrofuran. The half-open circles represent the Z-scan experimental data, and the solid lines are the theoretical fitting curves: (a) data collected under the open-aperture configuration; (b) data collected under the closed-aperture configuration.

UV–vis studies proved that this was indeed the case. Meanwhile, UV–vis spectra were enlarged with end-absorptions into the near infrared region, indicating excellent nonlinear optical properties. Furthermore, Z-scan measurements to investigate the third-order NLO properties confirmed that the 'click' C_{60} derivatives have excellent nonlinear absorptive and refractive properties. The present study opens up a venue for utilization of energy level tunable fullerene derivatives in nonlinear optics.

4. Experimental section

4.1. General

Reagents were purchased from commercial sources (Aldrich) and used without further purification. ¹H NMR spectra were measured on a Bruker AV300 NMR spectrometer (300 MHz) at 20 °C. Chemical shifts are reported in ppm downfield from SiMe₄, using the solvent's residual signal as an internal reference. FTIR was recorded on a Perkin Elmer LR-64912C Fourier transform infrared spectrometer. All MALDI-TOF-MS spectra were measured on a Shimadzu AXIMA-CFR mass spectrometer. The operation was performed at an accelerating potential of 20 kV by a linear positive ion mode with dithranol as a matrix. UV-vis spectra were recorded in a quartz cuvette on a JASCO V-570 spectrophotometer. Cyclic voltammetric measurements were carried out in a conventional threeelectrode cell using Glassy Carbon working electrodes of 2 mm diameter, a platinum wire counter electrode, and an Ag/AgCl reference electrode on a computer-controlled CHI 660C instrument at room temperature. The nonlinear optical properties (NLO) response was measured by means of Z-scan technique, employing 20 ps laser pulses at 532 nm delivered by a mode-locked Nd:YAG laser.

4.1.1. 2-(4-(Dibutylamino) phenyl)-3-(4-formylphenyl) buta-1,3diene-1,1,4,4-tetracarbonitrile (**C1**). The click monomer (0.0837 g, 0.250 mmol) and click reagent TCNE (0.032 g, 0.250 mmol) were dissolved in dichlorobenzene (10 mL). The reaction mixture was then stirred at 30 °C for 1 h under argon atmosphere. The mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed in vacuo and the crude product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **C1** (0.103 g, 90%) as a brown solid. ¹H NMR (CDCl₃, 300 MHz): δ =0.97 (6H, t), 1.38 (4H, m), 1.61 (4H, m), 3.92 (4H, t), 6.68 (2H, d, *J*=9.2), 7.76 (2H, d, *J*=9.6), 7.85 (2H, d, *J*=8.4), 8.01(2H, d, *J*=8.8), 10.08 (1H, s) ppm. FTIR (KBr, cm⁻¹): *v*=2957, 2872, 2727, 2206, 1698, 1597, 1523, 1466, 1402, 1369, 1284, 1207, 1165, 1134, 927, 830, 816, 518. MALDI-TOF-MS (dithranol): *m/z*: calcd for C₂₉H₂₇N₅O: 461.6 g mol⁻¹, found: 461.2 g mol⁻¹ [MH]⁺; elemental analysis calcd (%) for $C_{29}H_{27}N_5O$ (461.6): C 75.46, H 5.90, N 15.17; found: C 75.49, H 5.90, N 15.19.

4.1.2. 2-(1-(4-(Dibutylamino) phenyl)-2-(4-(dicyanomethylene) cyclohexa-2,5-dien-1-ylidene)-2-(4-formylphenyl) ethylidene) malononitrile (C2). The click monomer (0.0837 g, 0.250 mmol) and click reagent TCNQ (0.051 g, 0.250 mmol) were dissolved in dichlorobenzene (10 mL). The reaction mixture was then stirred at 50 °C for 3 h under argon atmosphere. The mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed in vacuo and the crude product was purified by column chromatography (SiO₂, ethyl acetate/petroleum ether=1:3) to give **C2** (0.122 g, 91%) as a yellow-brown solid. ¹H NMR (CDCl₃, 300 MHz): δ =0.96 (6H, t), 1.34 (4H, m), 1.57 (4H, m), 3.35 (4H, t), 6.64 (2H, d, J=9.2), 7.24 (4H, m), 7.53 (2H, d, J=8.8), 7.77 (2H, d, J=8.4), 7.95 (2H, d, J=8.4), 10.04 (1H, s) ppm. FTIR (KBr, cm⁻¹): *v*=2958, 2930, 2201, 1699, 1584, 1523, 1400, 1348, 1292, 1209, 1186, 1110, 920, 888, 825, 795, 682. MALDI-TOF-MS (dithranol): m/z: calcd for C₃₅H₃₁N₅O: 537.7 g mol⁻¹, found: 537.3 g mol⁻¹ [MH]⁺; elemental analysis calcd (%) for C₃₅H₂₇F₄N₅O (537.7): C 78.19, H 5.81, N 13.03; found: C 78.21, H 5.82, N 13.04.

4.1.3. 2-(1-(4-(Dibutylamino) phenyl)-2-(4-(dicyanomethylene)-2,3,5,6-tetrafluorocyclohexa-2,5-dien-1-ylidene)-2-(4-formylphenyl) ethylidene)malononitrile (C3). The click monomer (0.0837 g, 0.250 mmol) and click reagent F4-TCNQ (0.069 g, 0.250 mmol) were dissolved in dichlorobenzene (10 mL). The reaction mixture was then stirred at 80 °C for 3 h under argon atmosphere. The mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed in vacuo and the crude product was purified by column chromatography (SiO₂, ethyl acetate/petroleum ether=1:2) to give C3 (0.137 g, 90%) as a black solid. ¹H NMR (CDCl₃, 300 MHz): δ =0.86 (6H, t), 1.23 (4H, m), 1.42 (4H, m), 3.57 (4H, m), 6.81 (2H, d, J=8.8), 7.24 (2H, m), 7.72 (2H, d, J=7.6), 7.99 (2H, d, *J*=6.4), 10.07 (1H, s) ppm. FTIR (KBr, cm⁻¹): *v*=2959, 2872, 2190, 2147, 1701, 1639, 1600, 1520, 1482, 1393, 1290, 1196, 970, 826, 747. MALDI-TOF-MS (dithranol): m/z: calcd for C₃₅H₂₇F₄N₅O: 609.6 g mol⁻¹, found: 609.2 g mol⁻¹ $[MH]^+$; elemental analysis calcd (%) for C35H27F4N5O (609.6): C 68.96, H 4.46, N11.49; found: C 68.99, H 4.46, N 11.47.

4.1.4. 'Click' C_{60} derivative **S1**. A mixture of C_{60} (115 mg, 0.16 mmol) and sarcosine (13 mg, 0.15 mmol) was dissolved in 10 mL of *o*-DCB under argon atmosphere at 60 °C. Afterward, a solution of **C1** (69 mg, 0.15 mmol) in 5 mL of *o*-DCB was added. The reaction

mixture was heated at 110 °C for an additional 8 h. After being cooled to room temperature the solvent was evaporated. Unreacted C_{60} was eluted with methylbenzene. The crude was purified by column chromatography on silica gel. The mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed in vacuo and the crude product was purified by column chromatography (SiO₂, ethyl acetate/petroleum ether=1:1) to give **S1** (67 mg, 37%) as a black solid. ¹H NMR (CDCl₃, 300 MHz): δ=0.83 (6H, m), 0.96 (4H, m), 1.41 (4H, m), 1.68 (4H, m), 2.82 (1H, s), 4.28 (5H, m), 7.50₆ (2H, d, *J*=6.0), 7.51₄ (2H, d, *J*=5.6), 7.69 (2H, d, *I*=5.6), 7.70 (2H, d, *I*=5.7) ppm. FTIR (KBr, cm⁻¹): v=2959, 2212, 1720, 1602, 1535, 1485, 1451, 1415, 1342, 1262, 1209, 1183, 1098, 1019, 810, 705, 575, 527. MALDI-TOF-MS (dithranol): m/ z: calcd for C₉₁H₃₂N₆: 1209.27 g mol⁻¹, found: 1209.46 g mol⁻¹ $[MH]^+$; elemental analysis calcd (%) for C₉₁H₃₂N₆ (1209.27): elemental analysis calcd (%) for C₉₁H₃₂N₆ (1209.27): C 90.38, H 2.67, N 6.95; found: C 90.40, H 2.67, N 6.92.

4.1.5. 'Click' C₆₀ derivative **S2**. A mixture of C₆₀ (115 mg, 0.16 mmol) and sarcosine (13 mg, 0.15 mmol) was dissolved in 10 mL of o-DCB under argon atmosphere at 60 °C. Afterward, a solution of C2 (81 mg, 0.15 mmol) in 5 mL of o-DCB was added. The reaction mixture was heated at 120 °C for an additional 10 h. After being cooled to room temperature the solvent was evaporated. Unreacted C₆₀ was eluted with toluene. The crude was purified by column chromatography on silica gel. The mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed in vacuo and the crude product was purified by column chromatography (SiO₂, ethyl acetate/petroleum ether=3:1) to give **S2** (50 mg, 26%) as a dark brown solid. ¹H NMR (CDCl₃, 300 MHz): δ =0.86 (6H, m), 0.94 (4H, m), 1.23 (4H, m), 1.98 (4H, m), 2.19 (2H, m), 2.83 (1H, s), 4.28 (3H, m), 5.28 (4H, m), 7.52 (4H, m), 7.70 (4H, m) ppm. FTIR (KBr, cm⁻¹): v=2955, 2201, 1722, 1580, 1463, 1398, 1347, 1288, 1179, 923, 823, 527. MALDI-TOF-MS (dithranol): m/z: calcd for C₉₇H₃₆N₆: 1285.36 g mol⁻¹, found: 1285.30 g mol⁻¹ [MH]⁺; elemental analysis calcd (%) for $C_{97}H_{36}N_6$ (1285.36): C 90.64, H 2.82, N 6.54; found: C 90.61, H 2.83, N 6.53.

4.1.6. 'Click' C_{60} derivative **S3**. A mixture of C_{60} (115 mg, 0.16 mmol) and sarcosine (13 mg, 0.15 mmol) was dissolved in 10 mL of *o*-DCB under argon atmosphere at 60 °C. Afterward, a solution of **C3** (91 mg, 0.15 mmol) in 5 mL of *o*-DCB was added. The reaction mixture was heated at 140 °C for an additional 13 h. After being cooled to room temperature the solvent was evaporated. Unreacted C_{60} was eluted with methylbenzene. The crude was purified by column chromatography on silica gel. The mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed in vacuo and the crude product was purified by column chromatography (SiO₂, ethyl acetate/petroleum ether=3:1) to give **S3** (30 mg, 15%) as a black solid. ¹H NMR (CDCl₃, 300 MHz): δ =0.86 (6H, m), 0.96 (4H, m), 1.41 (4H, m), 1.68 (4H, m), 3.57 (6H, m), 7.44 (2H, d, *J*=6.0), 7.51 (2H, d, *J*=5.8), 7.72 (2H, d,

J=6.0), 7.79 (2H, d, *J*=5.7) ppm. FTIR (KBr, cm⁻¹): ν =2959, 2931, 2873, 2189, 1726, 1646, 1601, 1521, 1465, 1386, 1287, 1188, 1122, 1075, 1039, 801, 744, 705, 574, 527. MALDI-TOF-MS (dithranol): *m/z*: calcd for C₉₇H₃₂F₄N₆: 1357.33 g mol⁻¹, found: 1357.27 g mol⁻¹ [MH]⁺; elemental analysis calcd (%) for C₉₇H₃₂F₄N₆ (1357.33): C 85.83, H 2.38, N 6.19; found: C 85.87, H 2.39, N 6.20.

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Supplementary data

Cycle voltammograms and UV–vis spectra of 'click' compounds **C1–C3**. Measurement of third-order nonlinear optical and the corresponding parameters calculation. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.12.018.

References and notes

- (a) Zhou, G. J.; Zhang, S.; Wu, P. J.; Ye, C. Chem. Phys. Lett. 2002, 363, 610–614;
 (b) Zhou, G. J.; Zhang, S.; Ye, C. J. Phys. Chem. B 2004, 108, 3975–3984; (c) Spangler, C. W. J. Mater. Chem. 1999, 9, 2013–2020.
- (a) Correa, D. S.; De Boni, L.; Balogh, D. T.; Mendonca, C. R. *Adv. Mater.* 2007, *19*, 2653–2656; (b) Ambrosio, A.; Orabona, E.; Maddalena, P.; Camposeo, A.; Polo, M.; Neves, A. A. R.; Pisignano, D.; Carella, A.; Borbone, F.; Roviello, A. *Appl. Phys. Lett.* 2009, *94* 011115-(1-3).
- 3. Wang, C.; Zhang, T.; Lin, W. Chem. Rev. 2011, 112, 1084-1104.
- 4. Ruoff, R. S.; Malhotra, R.; Huestis, D. L.; Tse, D. S.; Lorents, D. C. *Nature* **1993**, 362, 140–141.
- (a) Deak, D. S.; Silly, F.; Porfyrakis, K.; Castell, M. R. J. Am. Chem. Soc. 2006, 128, 13976–13977; (b) Nakanishi, T.; Miyashita, N.; Michinobu, T.; Wakayama, Y.; Tsuruoka, T.; Ariga, K.; Kurth, D. G. J. Am. Chem. Soc. 2006, 128, 6328–6329.
- 6. Fournier, D.; Hoogenboom, R.; Schubert, U. *Chem. Soc. Rev.* 2007, 36, 1369–1380.
- (a) Zhou, G. J.; Wong, W. Y.; Cui, D. M.; Ye, C. Chem. Mater. 2005, 17, 5209–5217;
 (b) Wang, D.; Michinobu, T. J. Polym. Sci., Part A: Polym. Chem. 2011, 49, 72–81.
- 8. Prato, M.; Maggini, M. Acc. Chem. Res. 1998, 31, 519-526.
- Marta, C.; Salavagione, H.; Segura, J. L. *Org. Lett.* 2012, *14*, 2798–2801.
 Amin, A. N.; El-Khouly, M. E.; Subbaiyan, N. K.; Zandler, M. E.; Fukuzumi, S.; D'Souza, F. *Chem. Commun.* 2012, 206–208.
- 11. Sun, Y. P.; Lawson, G. E.; Riggs, J. E. J. Phys. Chem. A **1998**, 102, 5520–5528.
- (a) Reutenauer, P.; Kivala, M.; Jarowski, P. D.; Boudon, C.; Gisselbrecht, J. P.; Gross, M.; Diederich, F. *Chem. Commun.* **2007**, 4898–4900; (b) Varotto, A.; Nam, C. Y.; Radivojevic, I.; Tome, J. P. C.; Cavaleiro, J. A. S.; Black, C. T.; Drain, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 2552–2554.
- 13. Parr, R. G.; Yang, W. Annu. Rev. Phys. Chem. 1995, 46, 701-728.
- Zhang, Y.; Yip, H. L.; Acton, O.; Steven, K. H.; Alex, K. Y. J. Chem. Mater. 2009, 21, 2598–2600.
- 15. Li, Y. R.; Tsuboi, K.; Michinobu, T. Macromolecules 2010, 43, 5277-5286.
- Weaver, J. H.; Martins, J. L.; Komeda, T.; Chen, Y.; Ohno, T. R.; Kroll, G. H.; Troullier, N.; Haufler, R. E.; Smalley, R. E. Phys. Rev. Lett. 1991, 66, 1741–1744.
- Gong, Q. H.; Sun, Y. X.; Xia, Z. J.; Zou, Y. H.; Gu, Z.; Zhou, X. H.; Qiang, D. J. Appl. Phys. 1992, 71, 3025–3026.
- Varanasi, P. R.; Jen, A. K. Y.; Chandrasekhar, J.; Namboothiri, I. N. N.; Rathna, A. J. Am. Chem. Soc, 1996, 118, 12443–12448.