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# PAPER



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### 1. Introduction

Fullerene  $(C_{60})$  and its derivatives have been employed to a considerable extent as excellent electron-acceptor materials in various optoelectronic devices (such as organic solar cells and field effect transistors).1-6 On the other hand, as typical  $\pi$ -conjugated molecules, fullerenes are also important building blocks for fabrication of functional supramolecular assemblies.7-10 It has been recognized that the performance of molecular device could be improved by fine molecular-tailoring and directed self-organization of  $\pi$ -conjugated units. In this regard, many efforts have been devoted to self-assembly of fullerenes to manipulating properties of fullerene-based materials.11-19 For example, several well-defined organized nano/ microstructures such as spheres,20 rods,21 wires,22 belts,23,24 whiskers,25,26 and sheets,27,28 have been fabricated from the pristine C<sub>60</sub>, which retain the intrinsic optoelectronic properties of fullerenes but the numbers of solvents owning enough

# Electronic and electrochemical properties as well as flowerlike supramolecular assemblies of fulleropyrrolidines bearing ester substituents with different alkyl chain lengths<sup>†</sup>

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A series of alkyl (methyl, ethyl, propyl, butyl) benzoate ester substituted fulleropyrrolidine derivatives (FP1– FP4) were synthesized and their electronic and electrochemical properties were investigated by means of absorption spectra, electronic structure calculation, and cyclic voltammetry (CV), respectively. The LUMO– HOMO energies and energy gaps of fullerene derivatives were estimated by the first reduction potential measured with CV combined with absorption spectra, which are consistent with those obtained from density functional theory (DFT) calculations. It was found that all fulleropyrrolidines showed very similar absorption spectra, orbital energies and redox behaviors, which are comparable with those of wellknown phenyl- $C_{61}$ -butyric acid methyl ester (PCBM). The flowerlike supramolecular architectures obtained from the self-assembly of FP1–FP4 in chloroform–alcohol mixture solvents were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). A lamellar structure with a *d*-spacing of 1.92–2.02 nm that depends on the molecular size, corresponding to the thickness of a bilayer structure, suggested a face-to-face conformation of the substituent of  $C_{60}$  and an interdigitation of the bare  $C_{60}$  side packing. These fulleropyrrolidines have high  $C_{60}$  content, are energetically PCBM-like, and are capable of forming complex flowerlike architectures, which provide fundamental insights into molecular design toward advanced fullerene materials.

> solubility for C60 are very limited (usually aromatic solvents and carbon disulfide). Alternatively, molecular-tailoring of fullerenes via attachment of proper substituent groups on periphery of C60 cage not only enhances its solubility in common organic solvents, which is benefit for solution processing in device fabrication, but also enables the regulation of self-assembly.<sup>29-44</sup> For example, various superstructures such as nanofibers, vesicles, flowerlike architectures have been achieved by fulleropyrrolidines bearing multiple alkyl chains.41-44 However, the attachment of bulky and insulating appends largely decreased  $C_{60}$  content (usually lower than 50%), leading to these chemically-modified fullerenes are less electronically active that is actually undesirable for their optoelectronic applications. Therefore, grafting small substituent groups on fullerene surface should be more promising due to high C60 content will be retained in these fullerene derivatives.<sup>45,46</sup> Recently, a small pyridine group equipped fulleropyrrolidine was reported to be capable of organizing into C<sub>60</sub>-rich and photoconductive flowerlike architectures, which retain high C<sub>60</sub> content (84%) and photoinduced carrier-transporting properties comparable with pristine C60.45 Furthermore, it was also found that the morphology of self-organized objects could also be tuned by the position of N-atom in pyridine group. This example provides a useful molecular design concept for construction of C<sub>60</sub>-rich

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Data of additional computation results for C<sub>60</sub> and PCBM at various basis sets, other molecular properties (ionization potential, electro affinity, electronegativity, global hardness, *etc.*) and MOs for fullerenes are available. See DOI: 10.1039/c4ra10654g



complex supramolecular assemblies *via* grafting a small substituent group on periphery of fullerene cage. Thus the design and synthesis of other small substituent attached fullerene derivatives to investigate their electronic properties and self-assembly would further provide fundamental insights into fullerene-containing materials.

In this work, by considering the molecular structure of wellknown fullerene derivative, phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM), a small benzoate ester substituent group was then grafted on C<sub>60</sub> to synthesize a series of alkyl (methyl, ethyl, propyl, butyl) benzoate ester-substituted fulleropyrrolidines (FP1-FP4, Scheme 1), and their electronic and electrochemical properties as well as self-assembly were investigated by means of absorption spectra, electronic structure calculation, cyclic voltammetry (CV), scanning electron microscopy (SEM) and Xray diffraction (XRD) analysis, respectively. It was found that the LUMO-HOMO levels of these fullerene derivatives estimated by the experiments and theoretical calculations, are energetically PCBM-like. All of these fulleropyrrolidines could organize into flowerlike architectures of lamellar structures with alkyl chain length dependent *d*-spacing. These small ester substituent attached fullerenes are high C<sub>60</sub> content (76-79%), energetically PCBM-like, and capable of forming flowerlike assemblies, which provide fundamental insights into molecular design toward advanced fullerene materials.

### 2. Experimental details

Absorption, <sup>1</sup>H NMR and mass spectra were recorded on a TU-1901 (Persee), Brucker Avance III (400 MHz) and MALDI-TOF-MS (AB Sciex 4700) spectrometer, respectively. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on a HITACHI TM-1000 and JEOL-2100 microscopes, respectively. X-Ray diffraction (XRD) patterns were obtained using a RIGAKU D/Max-2550 PC X-ray diffractometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) curves were measured using a CHI 660D electrochemical workstation (Chenhua, Shanghai). The CV and DPV curves were collected at room temperature under N<sub>2</sub> using a conventional three-electrode system (glassy carbon working electrode, Pt wire counter-electrode and Ag/Ag<sup>+</sup> quasi-reference electrode) in 0.1 M tetrabutylammonium tetrafluoroborate (*n*-Bu<sub>4</sub>NBF<sub>4</sub>) solution in 1,2-dichlorobenzene (*o*-DCB) at a potential scan rate of 100 mV s<sup>-1</sup>, where the reduction potentials were calibrated using ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple as internal standard. The geometries of fulleropyrrolidine derivatives were optimized by density functional theory (DFT) at the B3LYP/6-31G(d) level, and the orbital energy and orbital analysis were calculated at the PBEPBE/6-311G(d,p) level, with the Gaussian 09 program package.<sup>47</sup>

Fullerene  $C_{60}$  (99%) was purchased from XFNANO (Nanjing) and other reagents as well as solvents (AR) were obtained from Sinopharm Chemical Reagents Co. (Shanghai). Alkyl (methyl, ethyl, propyl, butyl) 4-formylbenzoates were prepared by esterification reaction from 4-formylbenzoic acid with the corresponding alcohols in the presence of thionyl chloride. Fulleropyrrolidine derivatives (FP1–FP4, Scheme 1) were synthesized by refluxing the toluene solution of  $C_{60}$ , sarcosine and the corresponding benzaldehyde according to the standard Prato reaction.<sup>48</sup>

1, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.12 (d, 2H, *J* = 8.0 Hz), 7.94 (br, 2H), 5.07 (br, 2H), 4.33 (d, 1H, *J* = 8.0 Hz), 3.91 (s, 3H), 2.85 (s, 3H). MALDI-TOF-MS [DCTB] *m*/*z* calcd, C<sub>71</sub>H<sub>13</sub>NO<sub>2</sub> 911.23; found, 911.12.

2, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.13 (d, 2H, J = 8.0 Hz), 7.96 (br, 2H), 5.11 (br, 2H), 4.40–4.35 (m, 3H), 2.88 (s, 3H), 1.39 (t, 3H, J = 8.0 Hz). MALDI-TOF-MS [DCTB] m/z calcd, C<sub>72</sub>H<sub>15</sub>NO<sub>2</sub> 925.25; found, 925.76.

3, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.12 (d, 2H, J = 8.0 Hz), 7.92 (br, 2H), 5.05 (br, 2H), 4.33–4.25 (m, 3H), 2.84 (s, 3H), 1.82–1.76 (m, 2H), 1.03 (t, 3H, J = 8.0 Hz). MALDI-TOF-MS [DCTB] m/z calcd, C<sub>73</sub>H<sub>17</sub>NO<sub>2</sub> 939.28; found, 939.86.

4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.13 (d, 2H, *J* = 8.0 Hz), 7.97 (br, 2H), 5.12 (br, 2H), 4.37–4.30 (m, 3H), 2.88 (s, 3H), 1.79– 1.71 (m, 2H), 1.51–1.45 (m, 2H), 0.98 (t, 3H, *J* = 8.0 Hz). MALDI-TOF-MS [DCTB] *m*/*z* calcd, C<sub>74</sub>H<sub>19</sub>NO<sub>2</sub> 953.31; found, 953.87.

### 3. Results and discussion

#### 3.1. Photophysical properties

The absorption spectra (400–750 nm) of fulleropyrrolidine derivatives **FP1–FP4** in chloroform  $(1.3 \times 10^{-4} \text{ M})$  were shown

in Fig. 1, together with the spectrum of pristine  $C_{60}$  (6.5  $\times$  10<sup>-5</sup> M) for comparison. All of fulleropyrrolidine derivatives exhibit nearly the same broad absorption bands from 400 to 750 nm those extend to longer wavelength range than that of the pristine  $C_{60}$  (Fig. 1). The difference of photophysical properties between FP1-FP4 and the pristine C60 could be explained from the symmetry breaking effect in the former that enhanced the forbidden transitions to some extent.49 It was noted that the fulleropyrrolidine derivatives have stronger visible light absorption in the red-shifted absorption edge above 650 nm with the longer  $\lambda_{\text{onset}}$  around 724 nm (Table 1), which is similar to that of PCBM and important to contribute the light harvesting in photovoltaics.31 The similar absorption spectra observed among fulleropyrrolidine derivatives FP1-FP4 indicated that the alkyl chain length scarcely affects their photophysical properties.



Fig. 1 Absorption spectra of fulleropyrrolidines FP1–FP4 and the pristine  $\rm C_{60}$  in chloroform.

Table 1 Redox properties, energy gaps, LUMO and HOMO energy levels of fullerenes FP1–FP4, PCBM and the pristine  $C_{60}$ 

Parameters	C <sub>60</sub>	PCBM	FP1	FP2	FP3	FP4
n ( [1]	0 77	a aah	0.04	0.05	0.05	0.02
$E_1^{-1}[V]$	-0.75	$-0.90^{\circ}$	-0.84	-0.85	-0.85	-0.83
$E_2^a [V]$	-1.14	$-1.31^{h}$	-1.24	-1.24	-1.25	-1.23
$E_3^a$ [V]	-1.60	$-1.85^{h}$	-1.77	-1.77	-1.78	-1.76
$E_{\text{onset}}^{\text{red}\ b}$ [V]	-0.68	$-0.77^{h}$	-0.77	-0.78	-0.78	-0.78
$LUMO^{c}$ [eV]	-3.92	-3.83	-3.83	-3.82	-3.82	-3.82
$LUMO^{d}$ [eV]	-4.18	-4.00	-4.02	-4.01	-4.01	-4.01
$\lambda_{\text{onset}}^{e}$ [nm]	693	723	724	724	724	724
$E_{\rm gap}^{f}$ [eV]	1.79	1.72	1.72	1.72	1.72	1.72
$E_{\text{gap}}^{d}$ [eV]	1.69	1.52	1.50	1.50	1.50	1.50
HOMO <sup>g</sup> [eV]	-5.71	-5.55	-5.55	-5.54	-5.54	-5.54
HOMO <sup>d</sup> [eV]	-5.87	-5.52	-5.52	-5.51	-5.51	-5.51

<sup>*a*</sup> Half-wave potential. <sup>*b*</sup> Onset reduction potential. <sup>*c*</sup> LUMO =  $-e(E_{\text{onset}}^{\text{red}} + 4.60)$ . <sup>*d*</sup> Values from the DFT calculation. <sup>*e*</sup> Onset absorption wavelength. <sup>*f*</sup> Band gap =  $hc/\lambda_{\text{onset}}$  converted [J] to [eV]; *h*, Planks constant; *c*, speed of light. <sup>*g*</sup> HOMO = LUMO -  $E_{\text{gap}}$  [eV]. <sup>*h*</sup> Taken from ref. 55.

#### 3.2. Electrochemical properties

It is well-known that fullerenes have rich electrochemical property and can accept up to six electrons in solution.<sup>50,51</sup> The first reduction potentials of fullerene acceptors were usually used to estimate their lowest unoccupied molecular orbital (LUMO) energy, which determines the open circuit voltage performance of polymer solar cells together with the highest occupied molecular orbital (HOMO) energy levels of electron donor.52-54 We therefore measured the cyclic voltammograms of **FP1–FP4** and the pristine  $C_{60}$  for a comparison. As shown in Fig. 2, a series of cyclic voltammograms shows that three welldefined and reversible redox waves are retained in the functionalized fullerenes ranging from 0 to -2.6 V vs. Ag/Ag<sup>+</sup>, under room temperature and anhydrous air-free conditions, relative to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) internal standard. As shown in Fig. 3, three sharp and equal intensity peaks together with the noticeable fourth peaks were clearly observed from differential pulse voltammetry (DPV), further revealing that FP1-FP4 are typical redox-reversible fullerene derivatives. From the CV, it can be noted that three reversible redox peaks of all derivatives FP1-FP4 are all shifted to negative potentials by ca. 100 mV as compared to those of C<sub>60</sub>, an indication of the stronger electron acceptor. The measured half-wave potentials are listed in Table 1 together with the LUMO energy levels of the fullerene derivatives, estimated from the their onset reduction potentials  $(E_{\text{onset}}^{\text{red}})$  according to the equation, LUMO (eV) =  $-e(E_{\text{onset}}^{\text{red}} +$ 4.60).<sup>55</sup> The  $E_{\text{onset}}^{\text{red}}$  of **FP1-FP4** were -0.77, -0.78, -0.78, and -0.78 V, corresponding to the LUMO energy levels of -3.83, -3.82, -3.82, and -3.82 eV, respectively (Table 1), indicating the alkyl chain length has a little effect on their electrochemical properties. The LUMO energy levels of FP1-FP4 are ca. 0.1 eV higher than that of  $C_{60}$  (-3.92 eV), which is desirable for an electron acceptor in polymer solar cells to get higher opencircuit voltage.52-54 The redox properties, LUMO, HOMO and energy gap  $(E_{gap})$  of all derivatives are similar and also very close to those of PCBM (Table 1),55 an indicative of FP1-FP4 are PCBM-like electron acceptors.



Fig. 2 CV curves of fulleropyrrolidine derivatives FP1–FP4 and the pristine  $C_{60}$  in *o*-DCB.

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Fig. 3 DPV curves of fulleropyrrolidine derivatives FP1–FP4 in o-DCB. The parameters of DPV: amplitude, 0.05 V; pulse width, 0.2 s; sample width, 0.02 s; pulse period, 0.5 s.

#### 3.3. DFT calculations

To further understand the substituent effect on the LUMO-HOMO energy levels of fullerene acceptors, DFT calculations were performed by using the Gaussian 09 program package.47 Ground state geometrical structures of four fulleropyrrolidine derivatives FP1-FP4, PCBM and C<sub>60</sub> were optimized at the B3LYP/6-31G(d) level, and the molecular orbital energies were calculated at the more reliable PBEPBE/6-311G(d,p) level based on above optimized geometries.46,49,56,57 The calculated results are summarized in Table 1, and the schematic diagrams of HOMO and LUMO levels are shown in Fig. 4. It can be noted that the HOMO-LUMO energy gaps of fulleropyrrolidine derivatives FP1-FP4 reduced to 1.72 eV by comparison with 1.79 eV of C<sub>60</sub>, while their LUMO and HOMO energies are 0.17 and 0.35 eV higher than those of  $C_{60}$  (-4.18 and -5.87 eV), respectively (Fig. 4 and Table 1), which may explain the red-shifted absorption of substituted fullerenes. The calculated orbital energies of derivatives FP1-FP4 are nearly same as those of PCBM and also close to the experimental values (Table 1), confirming the PBE method a reliable in orbital energy calculation for fullerene systems. In addition, other molecular properties, such as molecular hardness, electrophilicity, electronegativity, etc., have also been provided (Table S2, ESI<sup>+</sup>). Considering the molecular hardness, large value means a hard molecule with less global reactivity. It was noted that the



Fig. 4 Schematic diagrams of HOMO and LUMO energy levels of  $C_{60}$ , PCBM, and fulleropyrrolidine derivatives FP1–FP4 calculated at PBEPBE/6-311G(d, p) level.

fulleropyrrolidine derivatives FP1-FP4 have smaller hardness values (ca. 0.75 eV) than that of  $C_{60}$  (ca. 0.84 eV), revealing they are more reactive. Orbital analysis of HOMO and LUMO were also carried out for FP1-FP4, PCBM and C<sub>60</sub> at the PBEPBE/6-311G(d,p) level (Fig. 5). The fulleropyrrolidine derivatives FP1-FP4, PCBM and C<sub>60</sub> showed very similar orbital distributions, in which both the LUMO and HOMO are mainly located on the fullerene cage, respectively. But it can still be noted that the electron delocalization for fullerene derivatives are slightly weakened relative to C<sub>60</sub>, which has been attributed to symmetry breaking of C60 molecule by functionalization.49,56 It should be noted that C60 has 3-fold degenerated LUMOs and 5fold degenerated HOMOs (Fig. S1, ESI<sup>+</sup>), but the LUMO and HOMO of fulleropyrrolidine derivatives FP1-FP4 become nondegenerated (Table S3 and Fig. S2, ESI<sup>+</sup>). Further orbital analysis for other occupied and vacant MOs showed that the highest occupied and lowest vacant MOs localized on phenyl substituent are energetically far from the HOMO and LUMO of FP1-FP4 (Fig. S3-S6 and Table S3, ESI<sup>†</sup>), suggesting a little contribution to the frontier MOs. These findings suggest that the hybridization change (from sp<sup>2</sup> to sp<sup>3</sup>) of C<sub>60</sub> carbon atoms involved in connection with substituent, which modified the localization and the nature of HOMO and LUMO, also contribute to the observed substituent effect. The similar orbital distribution of fullerene derivatives may explain the similar electronic and electrochemical properties observed in absorption spectra and CV.

#### 3.4. Self-assembly

To demonstrate how the small alkyl benzoate ester substituent groups affect the packing of  $C_{60}$  molecules in solid state, the self-organized objects of **FP1–FP4** were further investigated by SEM, TEM and XRD. The self-organized objects were prepared by mixing the chloroform solution of **FP1–FP4** (1 mg ml<sup>-1</sup>) with 2-propanol or ethanol (10 : 1, v/v), then dropping on Si wafers and evaporating the solvent in a capped petri dish up to 1 h until dryness at room temperature. The assembled objects on Si wafers were directly used for SEM or XRD characterization, while they were scratched off and dispersed in EtOH for a TEM. Fig. 6 shows SEM and TEM images of self-organized architectures formed from **FP1–FP4** derivatives. It can be noted that flowerlike objects with size distribution around 2–8 µm were consisted of plate nanostructures (Fig. 6a–e), which was also confirmed by TEM (Fig. 6f). To get information on molecular



Fig. 5 LUMO (top) and HOMO (bottom) contours for  $C_{60}$ , PCBM, and fulleropyrrolidine derivatives FP1–FP4 calculated at PBEPBE/6-311G(d,p) level.



Fig. 6 SEM (a–e) and TEM (f) images of self-organized architectures of FP1–FP4 obtained from the mixture of chloroform–alcohol. (a) FP1 from chloroform–2-propanol; (b) FP2 from chloroform–2-propanol; (c) FP3 from chloroform–2-propanol; (d) FP4 from chloroform–ethanol; (e) and (f) FP4 from chloroform–2-propanol.

packing, the bulk flowerlike objects obtained from FP1-FP4 on Si wafer were further investigated by XRD (Fig. 7). As shown in Fig. 7, one intense diffraction peak appeared at around 5° accompanied by several weaker peaks at higher angle region in FP1-FP4 derivatives, resembling those previously observed in others fulleropyrrolidines.42-45,58 These peaks are therefore similarly attributed to the reflections of (001), (002) and (003) planes with a d-spacing value of 1.92, 1.95, 1.98 and 2.02 nm for FP1, FP2, FP3, and FP4, respectively, suggesting a lamellar structure. In addition, by comparison with the patterns obtained from the pristine C<sub>60</sub>, the residue peaks can be readily assigned to the reflections of (111), (220), (311) and (222) planes of a fcc structure with the average spacing of 0.8 nm (as indicated by asterisks in Fig. 7), suggesting a  $\pi$ - $\pi$  (C<sub>60</sub>/C<sub>60</sub>) interaction in the assemblies. By taking the molecular size of 1.3-1.5 nm of FP1-FP4 obtained from the DFT calculation, the d-spacing of 1.92-2.02 nm that depends their molecular sizes, corresponds well to the thickness of a bilayer structure, where a



Fig. 7 XRD patterns of flowerlike objects of FP1–FP4 obtained from the mixture of chloroform–2-propanol.

face-to-face conformation of the substituent of  $C_{60}$  and an interdigitation of the bare  $C_{60}$  side packed as suggested before.<sup>7,13,45,58</sup> These observations suggest that the smaller grafted group insufficiently disturbing the strong  $\pi$ - $\pi$  interactions between adjacent  $C_{60}$  molecules,<sup>13</sup> especially the strongest peaks from fcc packing were clearly noticed in the case of **FP1** (Fig. 7).

### 4. Conclusions

In conclusion, a series of small alkyl (methyl, ethyl, propyl, butyl) benzoate ester group substituted fulleropyrrolidine derivatives (FP1-FP4) were synthesized and their electronic and electrochemical properties as well as self-assembly were investigated by means of absorption spectra, DFT calculation, CV, SEM, TEM and XRD, respectively. The LUMO-HOMO energies of fullerene derivatives were estimated by the first reduction potential measured with CV combined with absorption spectra, which are in consistent with those obtained from DFT calculations. All fulleropyrrolidines FP1-FP4 showed the very similar absorption spectra, orbital energies and redox behaviors, which are comparable with those of well-known PCBM, indicating alkyl chain length has little effect on their electronic and electrochemical properties. The SEM investigation of self-assembly of FP1-FP4 in chloroform-alcohol solution mixture solvents showed that flowerlike supramolcular architectures can be facilely achieved. XRD analysis revealed that these flowerlike objects were lamellar structures with the *d*-spacing of 1.92–2.02 nm that depends on the molecular size of FP1-FP4, corresponding well to the thickness of a bilayer structure. This suggested a face-to-face conformation of the substituent of C60 and an interdigitation of the bare C<sub>60</sub> side packing fashion. The fulleropyrrolidines FP1-FP4 are high C<sub>60</sub> content (76-79%), energetically PCBM-like, and capable of forming complex flowerlike architectures, which provide fundamental insights into molecular design toward advanced fullerene materials and may find potential application in optoelectronics.

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### Notes and references

- 1 C. Yang, J. Y. Kim, S. Cho, J. K. Lee, A. J. Heeger and F. Wudl, *J. Am. Chem. Soc.*, 2008, **130**, 6444–6450.
- 2 J. L. Segura, N. Martín and D. M. Guldi, *Chem. Soc. Rev.*, 2005, 34, 31–47.
- 3 D. M. Guldi, B. M. Illescas, C. M. Atienza, M. Wielopolskia and N. Martín, *Chem. Soc. Rev.*, 2009, **38**, 1587–1597.
- 4 C.-Z. Li, H. L. Yip and A. K. Y. Jen, *J. Mater. Chem.*, 2012, 22, 4161–4177.
- 5 Y. J. He and Y. F. Li, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1970–1983.
- 6 Y.-Y. Lai, Y.-J. Cheng and C. S. Hsu, *Energy Environ. Sci.*, 2014, 7, 1866–1883.
- 7 M. J. Hollamby, M. Karny, P. H. H. Bomans, N. A. J. M. Sommerdjik, A. Saeki, S. Seki, H. Minamikawa, I. Grillo, B. R. Pauw, P. Brown, J. Eastoe, H. Möhwald and T. Nakanishi, *Nat. Chem.*, 2014, 6, 690–696.
- 8 H.-G. Li, J. Choi and T. Nakanishi, *Langmuir*, 2013, **29**, 5394–5406.
- 9 Y. Yamamoto, G. Zhang, W. Jin, T. Fukushima, N. Ishii, A. Saeki, S. Seki, S. Tagawa, T. Minari, K. Tsukagoshi and T. Aida, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 21051– 21056.
- 10 V. Georgakilas, F. Pellarini, M. Prato, D. M. Guldi, M. Melle-Franco and F. Zerbetto, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 5075–5080.
- 11 L. Sánchez, R. Otero, J. María Gallego, R. Miranda and N. Martín, *Chem. Rev.*, 2009, **109**, 2081–2091.
- 12 T. Nakanishi, Chem. Commun., 2010, 46, 3425-3436.
- H.-G. Li, S. S. Babu, S. T. Turner, D. Neher, M. J. Hollamby,
  T. Seki, S. Yagai, Y. Deguchi, H. Möhwald and
  T. Nakanishi, *J. Mater. Chem. C*, 2013, 1, 1943–1951.
- 14 H. Asanuma, H.-G. Li, T. Nakanishi and H. Möhwald, *Chem.– Eur. J.*, 2010, **16**, 9330–9338.
- 15 P. Heremans, D. Cheyns and B. P. Rand, Acc. Chem. Res., 2009, 42, 1740-1747.
- 16 A. J. Moulé and K. Meerholz, *Adv. Funct. Mater.*, 2009, **19**, 3028–3036.
- 17 L. K. Shrestha, Q. M. Ji, T. Mori, K. Miyazawa, Y. Yamauchi, J. P. Hill and K. Ariga, *Chem.-Asian J*, 2013, 8, 1662–1679.
- 18 S. S. Babu, H. Möhwald and T. Nakanishi, *Chem. Soc. Rev.*, 2010, **39**, 4021–4035.
- 19 Y.-F. Shen and T. Nakanishi, *Phys. Chem. Chem. Phys.*, 2014, 16, 7199–7204.
- 20 X. Zhang and M. Takeuchi, *Angew. Chem., Int. Ed.*, 2009, **48**, 9646–9651.

- 21 L. Wang, B. Liu, D. Liu, M. Yao, Y. Hou, S. Yu, T. Cui, D. Li, G. Zou, A. Iwasiewicz and B. Sundqvist, *Adv. Mater.*, 2006, 18, 1883–1886.
- 22 J. Geng, W. Zhou, P. Skelton, W. Yue, I. A. Kinloch, A. H. Windle and B. F. G. Johnson, *J. Am. Chem. Soc.*, 2008, 130, 2527–2534.
- 23 X. Zhang and X. D. Li, Chin. Chem. Lett., 2014, 25, 912-914.
- 24 L. Wei, J. Yao and H. Fu, ACS Nano, 2013, 7, 7573-7582.
- 25 K. Miyazawa, Y. Kuwasaki, A. Obayashi and M. Kuwabara, J. Mater. Res., 2002, 17, 83-88.
- 26 M. H. Nurmawati, P. K. Ajikumar, R. Renu, C. H. Sow and S. Valiyaveettil, *ACS Nano*, 2008, 2, 1429–1436.
- 27 M. Sathish, K. Miyazawa, J. P. Hill and K. Ariga, *J. Am. Chem. Soc.*, 2009, **131**, 6372–6373.
- 28 C. Park, H. J. Song and H. C. Choi, *Chem. Commun.*, 2009, 4803–4805.
- 29 D. Mi, H.-U. Kim, J.-H. Kim, F. Xu, S.-H. Jin and D. H. Hwang, *Synth. Met.*, 2012, **162**, 483–489.
- 30 H. Yu, H.-H. Cho, C.-H. Cho, K.-H. Kim, D. Y. Kim, B. J. Kim and J. H. Oh, *ACS Appl. Mater. Interfaces*, 2013, 5, 4865–4871.
- 31 Y. J. He, H.-Y. Chen, J. H. Hou and Y. F. Li, *J. Am. Chem. Soc.*, 2010, **132**, 1377–1382.
- 32 C.-Z. Li, S.-C. Chien, H.-L. Yip, C.-C. Chueh, F.-C. Chen, Y. Matsuo, E. Nakamura and A. K. Y. Jen, *Chem. Commun.*, 2011, 47, 10082–10084.
- 33 K.-H. Kim, H. Kang, S. Y. Nam, J. Jung, P. S. Kim, C.-H. Cho,
   C. Lee, S. C. Yoon and B. J. Kim, *Chem. Mater.*, 2011, 23, 5090–5095.
- 34 I. Riedel, E. von Hauff, J. Parisi, N. Martin, F. Giacalone and V. Dyakonov, *Adv. Funct. Mater.*, 2005, 15, 1979–1987.
- 35 N. Nakashima, T. Ishii, M. Shirakusa, T. Nakanishi, H. Murakami and T. Sagara, *Chem.-Eur. J.*, 2001, 7, 1766– 1772.
- 36 A. M. Cassell, C. L. Asplund and J. M. Tour, Angew. Chem., Int. Ed., 1999, 38, 2403–2405.
- 37 J.-F. Nierengarten, New J. Chem., 2004, 28, 1177-1191.
- 38 X. Y. Meng, Q. Xu, W. Q. Zhang, Z. A. Tan, Y. F. Li, Z. X. Zhang, L. Jiang, C. Y. Shu and C. R. Wang, ACS Appl. Mater. Interfaces, 2012, 4, 5966–5973.
- 39 A. L. Rosa, K. Gillemot, E. Leary, C. Evangeli, M. T. González, S. Filippone, G. Rubio-Bollinger, N. Agraït, C. J. Lambert and N. Martín, *J. Org. Chem.*, 2014, **79**, 4871–4877.
- 40 X. Y. Meng, G. Y. Zhao, Q. Xu, Z. A. Tan, Z. X. Zhang, L. Jiang, C. Y. Shu, C. R. Wang and Y. F. Li, *Adv. Funct. Mater.*, 2014, 24, 158–163.
- 41 T. Homma, K. Harano, H. Isobe and E. Nakamura, J. Am. Chem. Soc., 2011, **133**, 6364–6370.
- 42 T. Nakanishi, W. Schmitt, T. Michinobu, D. G. Kurth and K. Ariga, *Chem. Commun.*, 2005, 5982–5984.
- 43 T. Nakanishi, Y.-F. Shen, J.-B. Wang, H.-G. Li, P. Fernandes, K. Yoshida, S. Yagai, M. Takeuchi, K. Ariga, D. G. Kurth and H. Möhwald, *J. Mater. Chem.*, 2010, **20**, 1253–1260.
- 44 T. Nakanishi, K. Ariga, T. Michinobu, K. Yoshida, H. Takahashi, T. Teranishi, H. Möhwald and D. G. Kurth, *Small*, 2007, **3**, 2019–2023.

- 45 X. Zhang, T. Nakanishi, T. Ogawa, A. Saeki, S. Seki, Y. F. Shen, Y. Yamauchi and M. Takeuchi, *Chem. Commun.*, 2010, **46**, 8752–8754.
- 46 X. Zhang, L. X. Ma and X. D. Li, *Synth. Met.*, 2014, DOI: 10.1016/j.synthmet.2014.09.030.
- 47 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, I. E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, О. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, I. W. Ochterski, R. L. Martin, К. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2010.
- 48 M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798–9799.
- 49 H. Wang, Y. J. He, Y. F. Li and H. M. Su, *J. Phys. Chem. A*, 2012, **116**, 255–262.
- 50 T. Suzuki, Y. Maruyama, T. Akasaka, W. Ando, K. Kobayashi and S. Nagasel, *J. Am. Chem. Soc.*, 1994, **116**, 1359–1363.

- 51 M. Carano, T. D. Ros, M. Fanti, K. Kordatos, M. Marcaccio, F. Paolucci, M. Prato, S. Roffia and F. Zerbetto, *J. Am. Chem. Soc.*, 2003, **125**, 7139–7144.
- 52 C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 374–380.
- 53 M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, 18, 789–794.
- 54 F. B. Kooistra, J. Knol, F. Kastenberg, L. M. Popescu, W. Verhees, J. H. Kroon and J. M. Hummelen, *Org. Lett.*, 2007, **9**, 551–554.
- 55 G. D. Han, W. R. Collins, T. L. Andrew, V. Bulović and T. M. Swager, Adv. Funct. Mater., 2013, 23, 3061–3069.
- 56 X. Zhang and X. D. Li, Chin. Chem. Lett., 2014, 25, 501-504.
- 57 The comparison of the HOMO and LUMO energies as well as energy gaps of C<sub>60</sub> and PCBM calculated with various basis sets and experimental values were listed in Table S1 (ESI†). It showed that the PBEPBE/6-311G(d,p) basis set is more reliable than B3LYP/6-311G(d,p) for energy calculation based on geometry optimized with B3LYP/6-31G(d). Energies calculated from PBEPBE/6-311G(d,p) based on geometry optimized at the same level and at B3LYP/6-31G(d) level exhibited the comparable value but the former is more cost in computation time. Therefore, we selected the B3LYP/6-31G(d) level for geometry optimization but the PBEPBE/6-311G(d,p) for energy calculation by considering both reliability and computation cost.
- 58 S. S. Babu, A. Saeki, S. Seki, H. Möhwald and T. Nakanishi, *Phys. Chem. Chem. Phys.*, 2011, 13, 4830–4834.