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Organometallic Photovoltaics: A New and Versatile Approach for Harvesting Solar Energy Using Conjugated Polymetallaynes

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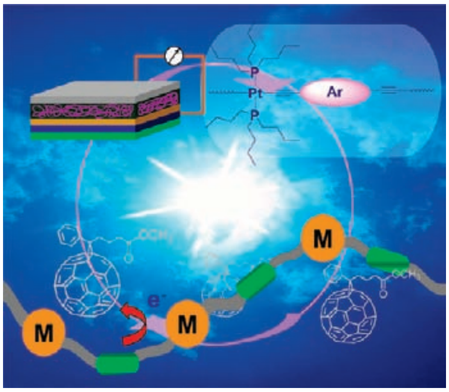

Energy remains one of the world's great challenges. Growing concerns about limited fossil fuel resources and the accumulation of CO_2 in the atmosphere from burning those fuels have stimulated tremendous academic and industrial interest. Researchers are focusing both on developing inexpensive renewable energy resources and on improving the technologies for energy conversion.

Solar energy has the capacity to meet increasing global energy needs. Harvesting energy directly from sunlight using photovoltaic technology significantly reduces atmospheric emissions, avoiding the detrimental effects of these gases on the environment. Currently inorganic semiconductors dominate the solar cell production market, but these materials require high technology production and expensive materials, making electricity produced in this manner too costly to compete with conventional sources of electricity. Researchers have successfully fabricated efficient organic-based polymer solar cells (PSCs) as a lower cost alternative. Recently, metalated conjugated polymers have shown exceptional promise as donor materials in bulk-heterojunction solar cells and are emerging as viable alternatives to the all-organic congeners currently in use. Among these metalated conjugated polymers, soluble platinum(II)-containing poly(arylene ethynylene)s of variable bandgaps (~1.4−3.0 eV) represent attractive candidates for a cost-effective, lightweight solar-energy conversion platform.

This Account highlights and discusses the recent advances of this research frontier in organometallic photovoltaics. The emerging use of low-bandgap soluble platinum−acetylide polymers in PSCs offers a new and versatile strategy to capture sunlight for efficient solar power generation. Properties of these polyplatinynes—including their chemical structures, absorption coefficients, bandgaps, charge mobilities, accessibility of triplet excitons, molecular weights, and blend film morphologies—critically influence the device performance. Our group has developed a novel strategy that allows for tuning of the optical absorption and charge transport properties as well as the PSC efficiency of these metallopolyynes. The absorbance of these materials can also be tuned to traverse the near-visible and near-infrared spectral regions. Because of the diversity of transition metals available and chemical versatility of the central spacer unit, we anticipate that this class of materials could soon lead to exciting applications in next-generation PSCs and other electronic or photonic devices. Further research in this emerging field could spur new developments in the production of renewable energy.

1. Introduction

A major global issue today is the upcoming depletion of fossil fuels and the energy crisis. While the quality of our life depends largely on the availability of energy, one of the grand challenges of this century is to develop innovative materials that would provide new sources of clean sustainable energy or to develop processes that can lead to efficient utilization of energy. Renewable energy

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sources such as solar, wind, and hydroelectric power can provide large amounts of energy to solve most of our immediate energy needs and fight for a cleaner environment.[1] The current global annual energy consumption was ∼13 TW, a majority of which came from fossil fuels. This translates into massive annual emissions of CO_2, bringing many detrimental environmental effects. Future global energy demand is projected to rise to ∼30 TW by 2050, which requires at least an extra 17 TW by 2050 when our fossil fuel reserves are vanishing.[2]

Solar energy is promising because the Earth receives more energy from the Sun in an hour than is necessary for all humanity within a year. The sun can supply abundant and noncontaminating clean energy. While photovoltaic production presents the world's fastest-growing energy technology, much research has gone into producing efficient solar (photovoltaic) cells.[3] Currently, solar cells are made largely from inorganic semiconductors (e.g., crystalline and amorphous Si and, recently, CdTe and $CuInGaSe_2$ thin films[3]) which have dominated the production market. Although these photovoltaic arrays can promise high efficiencies, they also require hi-tech production and are still too expensive to compete with conventional grid electricity. Complementary to the inorganic counterparts, organic solar cells (OSCs), which are simpler and less costly to manufacture, have recently shown great promise. OSCs, especially polymer solar cells (PSCs),[4] can be made flexible and translucent, are lightweight, and offer more opportunities for application in new markets such as mobile electronics, smart cards, power-generating windows, automotive, home appliances, etc. Their unique features also add a decorative and aesthetic dimension to the solar cells so that they can be used on curved and irregular surfaces, something that cannot be done using rigid Si solar cells. Organic photovoltaic materials are also chemically versatile and can be synthesized in large quantities under moderate conditions. Conjugated organic polymers are thus becoming eminent candidates for implementation in PSCs, which can be fabricated by solution-processing technologies and scaled up for production of large-area and mechanically flexible devices.[5]

2. Bulk-Heterojunction Polymer Solar cells

Bulk heterojunctions (BHJs) made from bicontinuous polymer—fullerene composites are currently the main configurations for highly efficient PSCs (Figure 1).[6] The hole-collection electrode consists of indium tin oxide (ITO) with a spin-coated poly(3,4-ethylene-dioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS), while Al serves as the electron-collecting electrode. Such protocol provides a route by which nearly all photogenerated excitons in the film can be split into free charge carriers. In inorganic semiconductors, the binding energy is usually small compared with the thermal energy at room temperature, thus favoring generation of photoinduced free charges under ambient conditions. However, the higher exciton binding energy of an organic semiconductor typically produces excitons instead of free charges upon photoexcitation.[7] Because PSCs require a mechanism to dissociate the excitons,[7] a donor—acceptor (D—A) interface is necessary to maximize the interfacial area between the two components and dissociate bound electron—hole pairs to generate free charges.[6] Photoinduced electron transfer (PET) and charge separation are key steps in BHJ cells.

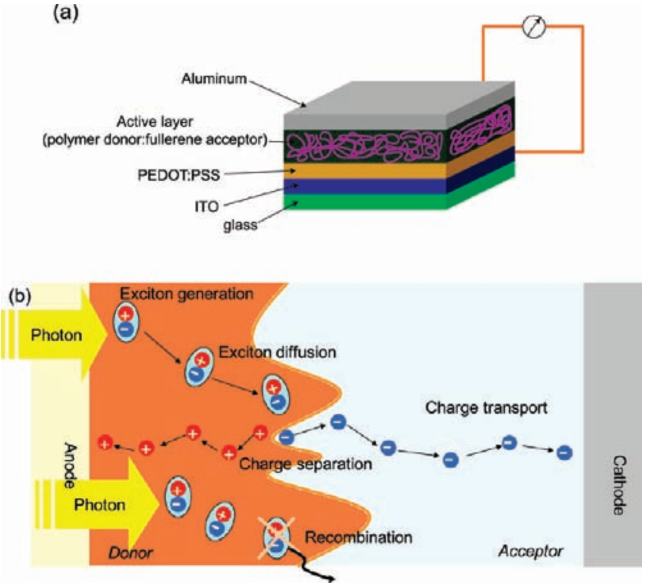


FIGURE 1. (a) General structure of a BHJ device and (b) key steps involved in a BHJ device.

Buckminsterfullerene (C_{60}) and its soluble derivative, [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), are promising electron acceptor materials known for OSCs/PSCs.[4] The state-of-the-art PSCs are represented by BHJs based on a phase-separated blend of PCBM and poly(3-hexylthiophene) (P3HT) with reproducible power conversion efficiency (PCE) approaching 5%.[8] To date, much effort has been devoted to developing new organic donor materials and establishing what their properties should be to afford efficient solar cells by blending with PCBM.[9] With different levels of optimization, the best PCE for PSCs has just exceeded 7%.[10]

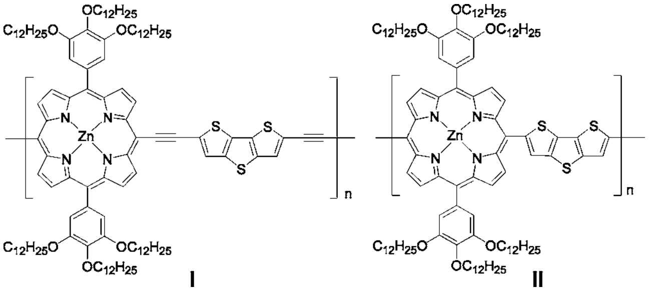


FIGURE 2. Zn(porphyrin)−dithienothiophene polymers with and without acetylene linkages.

3. Acetylene- and Metal-Containing Materials

3.1. Acetylene Linkage. The discovery of semiconducting polyacetylene set a milestone toward the field of organic optoelectronics. The development of efficient protocols for the Pd-catalyzed sp^2−sp alkynylation reactions and the concept of steric and conformational advantages of triple bonds render conjugated arylacetylenes (e.g., poly(arylene ethynylene)s)[4d,11] a novel class of semiconductors for OSCs/PSCs. In some recent studies, solar cells based on the acetylenic donors are more efficient than those for the olefinic donors.[12] This can be revealed from the higher PCE for the more rigid **I** than **II** (Figure 2), thanks to the stronger Q-band absorption and higher mobility observed for **I**.[12a]

3.2. Metal Coordination. Although organic polymers are still dominating the PSC field, their metal-containing derivatives represent another versatile class of molecular and polymeric semiconductors. Organometallic donors have become prevalent in small-molecule solar cells in which the Grätzel-type cell owes much success to this area.[13] The introduction of metal ions into conjugated polymers offers many advantages:[14] (1) the metal ions may act as architectural templates in the assembly of the organic subunits; (2) they may provide redox-active and paramagnetic centers to generate active species for charge transport and may greatly alter the electronic and optical properties of organic π-systems; (3) they allow fine-tuning of the HOMO−LUMO gap through the interaction of the metal d-orbitals with the ligand orbitals; (4) there is a diversity of molecular frameworks based on different coordination number, geometry and valence shells of different metal atoms. Among these, platinum(II) arylene ethynylenes are suitable building blocks,[14a,b] and the charge transport in Pt−acetylides has been demonstrated.[15] When Pt metal is conjugated with an alkyne unit, the Pt d-orbitals overlap with the p-orbitals of the alkyne unit, which leads to an enhancement of π-electron delocalization and intrachain charge transport along the main chain. Efficient intersystem crossing in such organometallic species by enhancing the spin−orbit coupling facilitates the formation of triplet excitons, which have longer lifetimes and thus allow extended exciton diffusion lengths. The generally good solubility of Pt-containing poly(heteroarylene ethynylene)s over their organic analogues also favors good film formation.

4. Solar-Energy Conversion Using Polyplatinynes

4.1. Bandgap Control. The first single-layer metallopolyyne photocells consisting of a neat Pt−phenylene polyyne ($E_g \approx$ 3.0 eV) gave photocurrent yield of up to ~0.6%.[16] The efficiency was raised to ~2% by adding 7 wt % C_{60}, and electrons are transferred from the Pt donor onto C_{60} by efficient ionization of the triplet exciton.[17] The photovoltaic application of wide-gap metallopolyynes is still less competitive than their lower-gap organic counterparts.[4]

Over the years, different research groups have developed a series of photovoltaic Pt polyynes with strong absorption throughout the visible region and tunable bandgaps (E_g) (Figures 3 and 4).[18] For low-gap polymers, the chromophores feature D−A intramolecular charge transfer (ICT) in which the D groups include thiophene, phenothiazine, (3,4-ethylenedioxy)-2,5-thiophene, and thieno[3,2-*b*]thiophene whereas the A groups can be 2,3-diheptylpyrido[3,4-*b*]pyrazine, 2,1,3-benzothiadiazole, thieno[3,4-*b*]pyrazine, and 4*H*-cyclopenta[2,1-*b*:3,4-*b′*]dithiophen-4-one. The addition of electron-withdrawing imine nitrogen can enhance its electron-accepting properties. The degree of ICT interaction between D and A moieties can be chemically modified, which increases with the acceptor strength (Figure 5). For **6**−**9**, **10**−**13**, and **14**−**16**, the E_g is lowered by increasing the number of thiophene rings (*m*), which improves spectral coverage of the solar spectrum.[18b,c] Very narrow E_g's were observed for **18**−**22** and **24**−**25**, even reaching near-infrared (NIR).[18e,g,h] The E_g of 1.44 eV for **25** is unprecedented and the lowest yet known for polyplatinynes.[18g]

4.2. Effect of Copolymerization. Random D−A copolymers with two different acceptors (**26**−**31**) were also reported (Figure 6).[18h] The absorption spectra of copolymers are similar in shape with distinct π−π^* and ICT absorption bands. Higher thieno[3,4-*b*]pyrazine content in **26** gives higher absorption intensity at shorter wavelength than **27**. Both **26** and **27** exhibit similar E_g to that of **20**, suggesting the more dominant contribution of the thiophene−thieno[3,4-*b*]pyrazine−thiophene pair. Likewise, **29** and **30** have very close E_g. Engineering of E_g and the relative intensity of two ICT

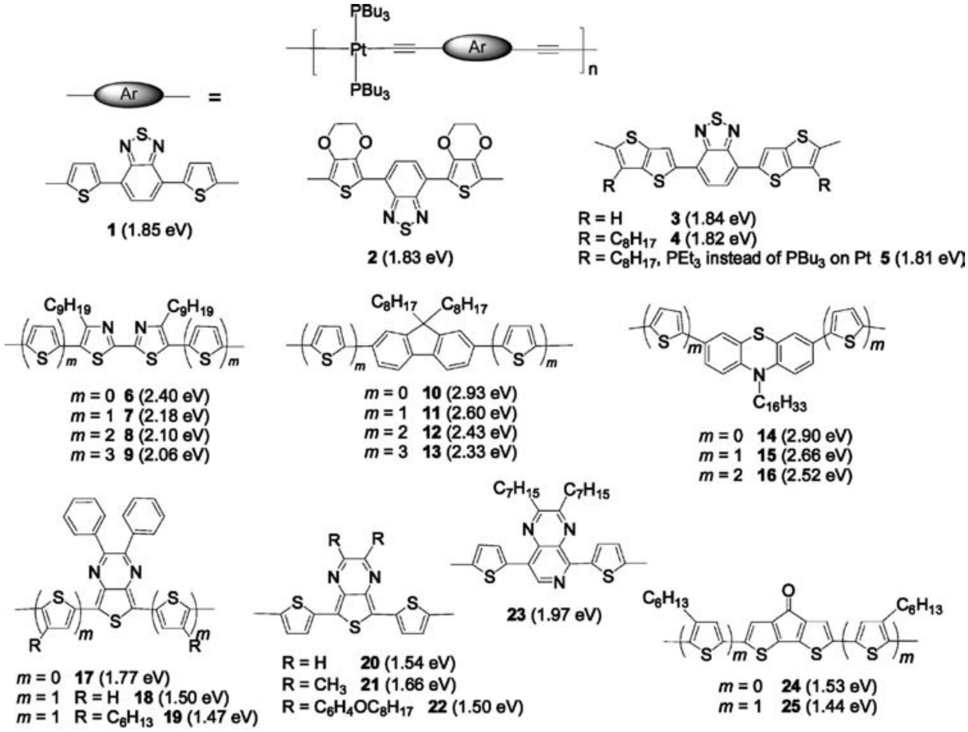


FIGURE 3. Some Pt polyynes of tunable bandgaps for PSCs (with E_g in parentheses).

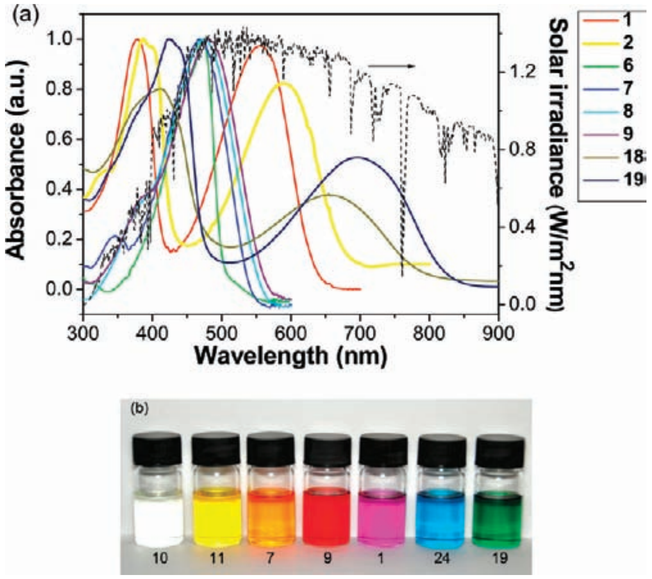


FIGURE 4. (a) Absorption spectra of representative polyplatinynes in CH_2Cl_2 spanning a wide spectral range relative to the standard AM 1.5 solar spectrum and (b) a picture showing the diversity of colors exhibited by Pt-polyynes.

bands due to different acceptors was demonstrated by varying the D−A−D pair and the composition of comonomer.

4.3. Effect of Triplet Excitons. The longer triplet-exciton lifetime would favor charge generation, but its higher binding energy than the singlet would make direct ionization of the triplet more difficult. Such trade-off issue determines whether a significant amount of charge carriers is formed.[19]

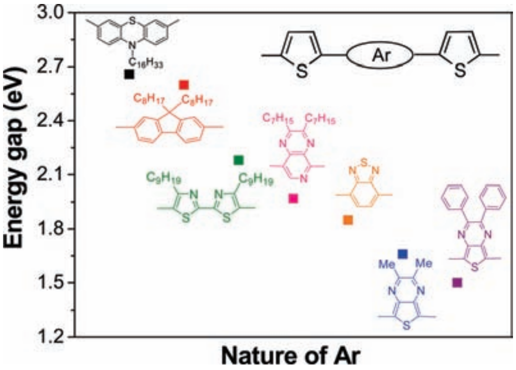


FIGURE 5. Tuning of E_g with different D−A combinations.

Indeed, triplet excitons were harnessed to increase the efficiency of charge generation in **32** and **33** (Figure 7).[20,21] While the long lifetime of the triplet may enhance the probability of exciton diffusion to the D−A interface, quantum-mechanical spin restrictions prevent spin-forbidden charge recombination in the geminate ion-radical pair produced as a result of PET from a spin-triplet precursor. A PCE of 0.27% was achieved in BHJ cells using the **32**:PCBM (1:4) composite.[20] The efficiency for generating long-lived charge separation was higher when the polymer excited state that preceded PET was a triplet state. However, the lack of effective absorption for **32** in the red to NIR regime of the solar spectrum was considered to account for the low PCE.

In another study, Schanze's group covalently linked a platinum−acetylide oligomer to two C_{60}-based acceptors in

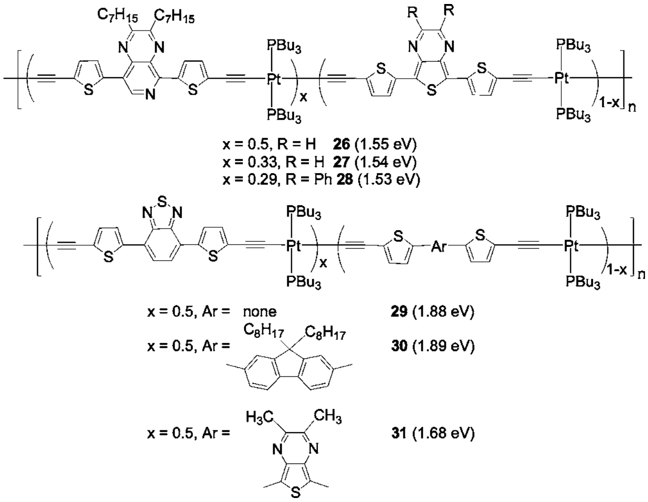


FIGURE 6. Six random platinum–acetylide copolymers (with E_g in parentheses).

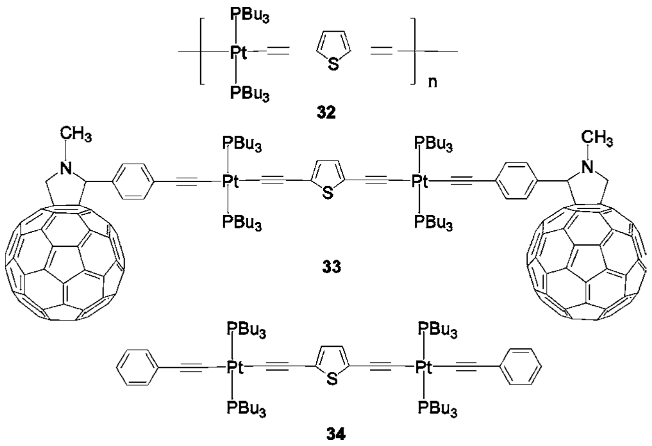


FIGURE 7. Chemical structures of **32**–**34**.

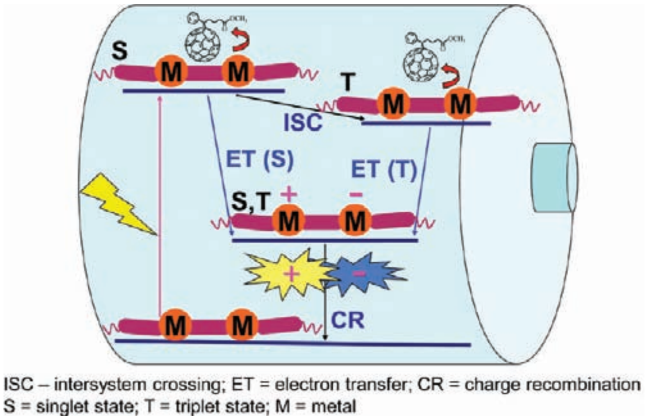


FIGURE 8. Energy level diagram showing the involvement of singlet and triplet states in PET for metallopolyynes.

33.[21] Such a triad would increase the PET efficiency and reduce the spatial separation of the D and A phases in BHJs. This approach identifies the role of triplet-state involvement in organometallic photovoltaics (Figure 8). The absorption profile of **33** is a linear sum of those from **34** and C_{60} moieties. For **33**, the triplet state of Pt–acetylide is efficiently quenched, presumably via PET to C_{60} ($C_{60}{-}^{3}[\mathbf{34}]^{*}{-}C_{60} \rightarrow C_{60}{-}[\mathbf{34}^{+\bullet}]{-}C_{60}^{-\bullet}$), suggesting that triplet state was active in charge generation. Photoexcitation of the **34**-derived unit in **33** is followed by very fast PET to produce the charge-separated state consisting of a mixture of singlet and triplet spin states. A solar cell based exclusively on **33** gave moderate PCE of 0.056% (PCQE ≈ 22%), which outperformed devices with **33**/PCBM and **34**/PCBM blends.

TABLE 1. Performance of Impressive BHJ Cells Fabricated from Polyplatinynes

	HOMO, LUMO, E_g (eV)	blend ratio (polymer/PCBM)^a	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	mean PCE (%)	ref
1	−5.37, −3.14, 1.85	1:4 (T)	0.82	13.1	0.37	4.10^c	18a
3	−5.18, −3.34, 1.84	$1:4^b$ (CF)	0.84	7.33	0.40	2.45	18i
4	−5.12, −3.30, 1.82	$1:4^b$ (CF)	0.81	8.67	0.51	3.57	18i
5	−5.14, −3.33, 1.81	$1:4^b$ (CF)	0.79	9.61	0.49	3.73	18i
8	−5.79, −3.69, 2.10	1:5 (T)	0.90	6.39	0.46	2.66	18b
9	−5.71, −3.65, 2.06	1:4 (T)	0.88	6.50	0.44	2.50	18b
12	−5.79, −3.87, 2.43	1:5 (CB)	0.94	4.05	0.56	2.11	18c
13	−5.73, −3.89, 2.33	1:5 (CB)	0.89	6.59	0.41	2.41	18c

[a] Solvent used for spin-casting in parentheses (T = toluene; CB = chlorobenzene; CF = chloroform). [b] $PC_{71}BM$ was used. [c] Independently verified (see Supporting Information in ref 18a).

4.4. Understanding and Optimizing Solar Cell Performance. 4.4.1. Recent Advances. PSC devices were fabricated using polymetallaynes as the electron donor and PCBM as the electron acceptor. Some promising results are gathered in Table 1. No phosphorescence could be observed for low-gap materials when high content of the heteroaryl component dilutes the heavy-metal effect. The singlet state was found to contribute to efficient PET in the photovoltaic energy conversion of low-bandgap polymers, which is different from higher-gap congeners such as **32** where charge separation takes place mostly via the triplet state.[16,17,20,21] Although the triplet is not involved in charge separation for low-gap polymers, it could influence the efficiency of charge separation indirectly by providing a pathway for direct charge recombination to the lower-lying triplet state.

4.4.2. Effect of Metalation. Comparison between metalated and metal-free polymers indicates a better photovoltaic performance for **1**, which possesses an additional metal-to-ligand charge-transfer absorption at ~582 nm (Figure 9), suitable for capturing a larger fraction of the solar flux. While the electron and hole transport was quite balanced in **1**,[18a] it was not the case in nonmetalated polymer, which gave higher charge recombination and lower PCE (~0.13%). However, blend-film phase separation is not necessarily affected by metal incorporation.

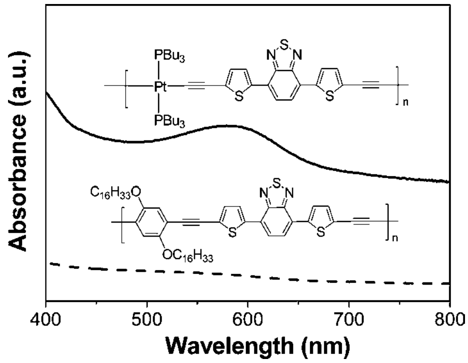


FIGURE 9. Absorption spectra of **1**/PCBM (with and without Pt) (1:4) at the same thickness of 75 nm.

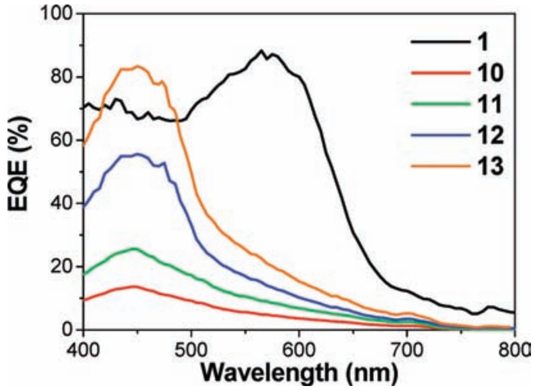


FIGURE 10. EQE wavelength dependencies of (a) **1**/PCBM (1:4) and (b) **10**−**13**/PCBM (1:5) blend solar cells.

4.4.3. Absorption Coefficient, Charge Mobility, and Ionization Potential.

For efficient solar cells, a key point with low-E_g polymers is the need not only for broadened absorption spectra but also for sufficiently high absorption coefficients and charge mobilities of the thin film and effective physical and electronic interactions with the fullerene components. Figure 10 shows the representative external quantum efficiency (EQE) wavelength dependencies of solar cells with **1**/PCBM (1:4) and **10**−**13**/PCBM (1:5) blends. The peak EQEs of **1**, **8**, **9**, **12**, and **13** are 87%, 81%, 59%, 56%, and 83%, respectively.[18a−c] Although charge separation occurred with good EQE, the overall performance was still limited by incomplete light-harvesting and low carrier mobility.

For **10**−**13**, the PCE increased sharply from **10** to **13** by increasing *m* from 0 to 3 due to the increasing optical absorbance (or extinction coefficient) and charge mobility, and the light-harvesting ability of **13** was increased by 8 times from that of **10**.[18c] The same trend was also observed in the series with bithiazole (**6**−**9**)[18b] and phenothiazine (**14**−**16**)[18f] units. The PCE of **9** (2.50%) was much increased relative to **6** (0.21%).[18b]

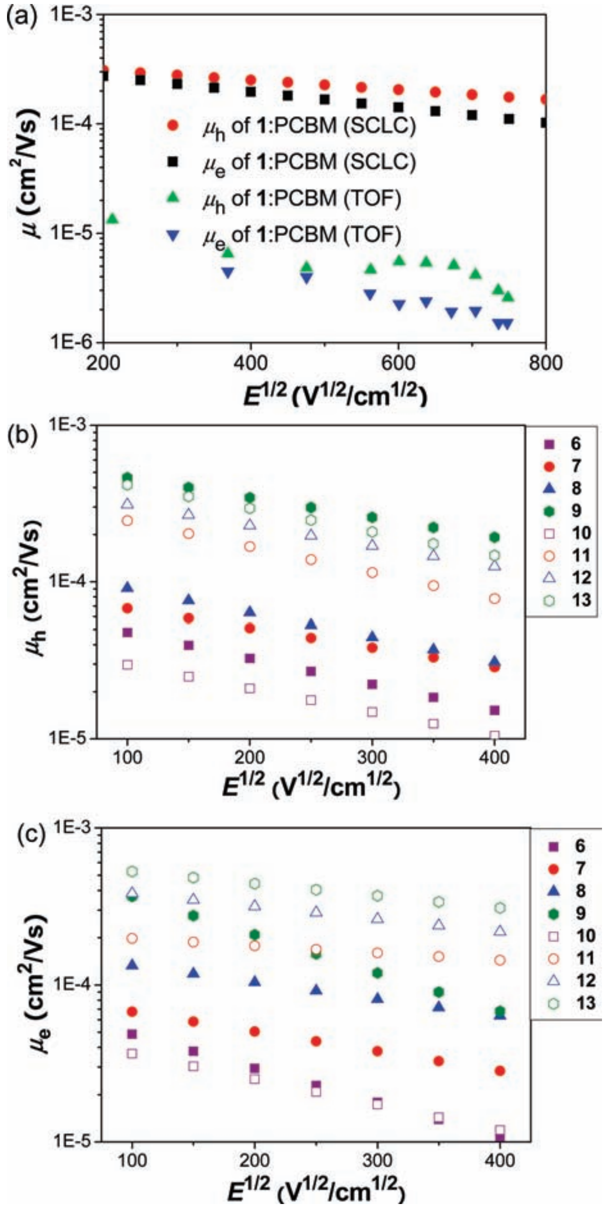


FIGURE 11. (a) The SCLC and TOF-computed hole (μ_h) and electron (μ_e) mobilities in **P1**/PCBM blends and comparisons between (b) μ_h and (c) μ_e in **6**−**13**/PCBM blends by SCLC modeling.

Charge transport in **1**/PCBM blend was studied using time-of-flight (TOF) and space-charge limited current (SCLC) techniques.[18a] The hole (μ_h) and electron (μ_e) mobilities were rather balanced for **1** (Figure 11a). Figure 11b,c shows the comparison between μ_h and μ_e in **6**−**9** and **10**−**13** blends. For both series, the mobilities increase with *m* because of more extended π-conjugation.[18b,c] It is likely that intrachain mobility contributes to the bulk properties. Also, an increasing trend for μ_h can be attributed to a better stabilization of the cationic species when the conjugation length is increased. Thus, not only optical but also charge transport properties can be tuned by changing *m*. The effect of absorption on PSC behavior was also probed by spectroscopic ellipsometry measurements for **1** and **6**−**9**.[18a,b] A **5**/$PC_{71}BM$ (1:4) system also

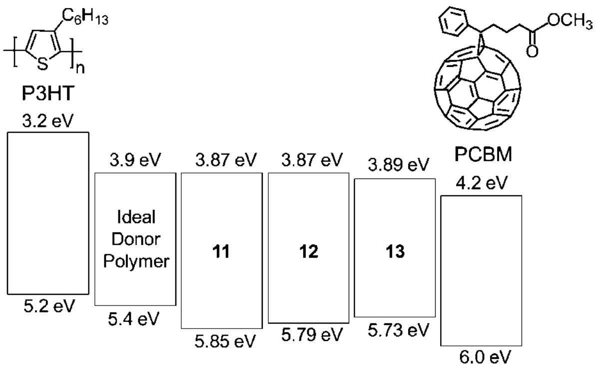


FIGURE 12. Band-structure diagram of **11**−**13**, P3HT, and an ideal donor relative to PCBM. Minus sign is omitted for energy values.

gave a peak PCE of 4.1%.[18i] The more rigid structure of alkyl-substituted thieno[3,2-*b*]thiophene and use of PEt_3 in **5** conferred to it an impressive μ_h. However, the low charge mobilities of **26**−**31** contributed to their poor performance.[18h]

The open-circuit voltage (V_{oc}) of the BHJ device was shown to correlate with the energy of the HOMO of the polymer (E_D) and the LUMO of the acceptor (E_A), according to[22]

$$V_{oc} = 1/e[E_D - E_A] - 0.3 \tag{1}$$

So, an effective method to improve V_{oc} is to manipulate the E_D (or ionization potential (IP)) by modifying the polymer structure. The same linear relationship was observed for E_A. A theoretical estimation predicts that a PCE of 10% could be achievable for single-layer cells from a polymer donor with a HOMO−LUMO gap of 1.74 eV.[9] A downhill LUMO energy offset of 0.3 eV between polymer and fullerene is required to effect the exciton splitting and charge dissociation for an ideal polymer.[23] A larger value than this offset would result in wasted energy that does not contribute to the device performance. The V_{oc} of **1** is higher compared with P3HT/PCBM cells (0.74 V), which is presumably due to the lower E_D of **1** (−5.37 eV versus −5.20 eV for P3HT).[18a] The E_A's of around −3.9 eV for **11**−**13** match well that of an ideal polymer, giving them very high V_{oc} (Figure 12).[18c] The V_{oc}'s of 0.66, 0.53, 0.52, and 0.39 V for **23**/$PC_{71}BM$ ($PC_{71}BM$ = [6,6]-phenyl-C_{71}-butyric acid methyl ester), **21**/$PC_{71}BM$, **18**/$PC_{71}BM$, and **20**/$PC_{71}BM$ cells, respectively, can be explained by their differences in IP.[18h] Similarly, the V_{oc}'s for the blends of **26**, **27**, and **31** with fullerene were quite similar (0.50−0.52 V) since their IPs are comparable and limited by the dominating thieno[3,4-*b*]pyrazine.[18h] The V_{oc} of **18** and **28** blends were even lower (0.39 and 0.32 V), which are primarily due to their much lower IPs, unfavorable molecular weight (MW), and poor p-channel semiconducting behavior.

4.4.4. Device Fabrication Parameters. Different processing methods can result in differences in BHJ morphology and consequently different device performance. Optimization of the processing procedure is expected to be dependent upon the solvent evaporation kinetics, viscosity effects, and shear stresses during solvent evaporation.[24] The solar cell efficiency depends on a number of interrelated factors to get the best values of V_{oc}, short-circuit current density (J_{sc}), and fill factor (FF). Since the PCE is defined as power output (P_{out}) divided by power input (P_{in}), changing each of the parameters would affect the overall performance, as exemplified in Figure 13 for **1**.[25]

$$\mathrm{PCE} = \frac{P_{out}}{P_{in}} = \frac{P_{max}}{P_{in}} = \frac{V_{max}J_{max}}{P_{in}} = \frac{V_{oc}J_{sc}\mathrm{FF}}{P_{in}} \tag{2}$$

$$\mathrm{FF} = \frac{V_{max}J_{max}}{V_{oc}J_{sc}} \tag{3}$$

The blend ratio is an important parameter in controlling the morphology and phase separation of the film. However, optimal blend concentration depends on the polymer used. For **1**:PCBM blend, there is about 4-fold improvement in PCE between the best efficiency (1:4) and the worst one (1:1) (Figure 13a).[18a,25]

The influence of casting solvent is likely related to the degree of roughness and topography of the film obtained by spin-coating. The size of the PCBM-rich domains in the blend film changes tremendously with the choice of solvent, which affects the phase separation and morphology. The blend film prepared from toluene and chlorobenzene solutions had a slow evaporation time compared with that from the chloroform solution, and a slower evaporation time results in a rougher film. The different solubilities of PCBM in different solvents also interfere with the phase separation of the film. The solvent effects were examined for **1** (Figure 13b), and there is a dramatic difference between the best (PCE = 4.3% for toluene) and the worst (PCE =1.2% for xylene) conditions. Results from Schanze's group also showed that different spin rates gave different device results for **1**.[26]

Generally, the optimal thickness of active layer represents a compromise between absorption and charge collection. A thicker layer will absorb more light, but increased thickness will result in a lower charge collection because of the low charge-carrier mobilities (Figure 13c).[27] When the cathode was changed, the V_{oc} had a difference of ~0.15 V between Al and Mg/Ag for **1**/PCBM blend (Figure 13d), because of the pinning of Fermi level of the electrodes to the reduction potential of PCBM.

An understanding of the complex interplay between the morphology and electronic properties of polymer film is necessary if the technology is to find viable application.[28] Opti-

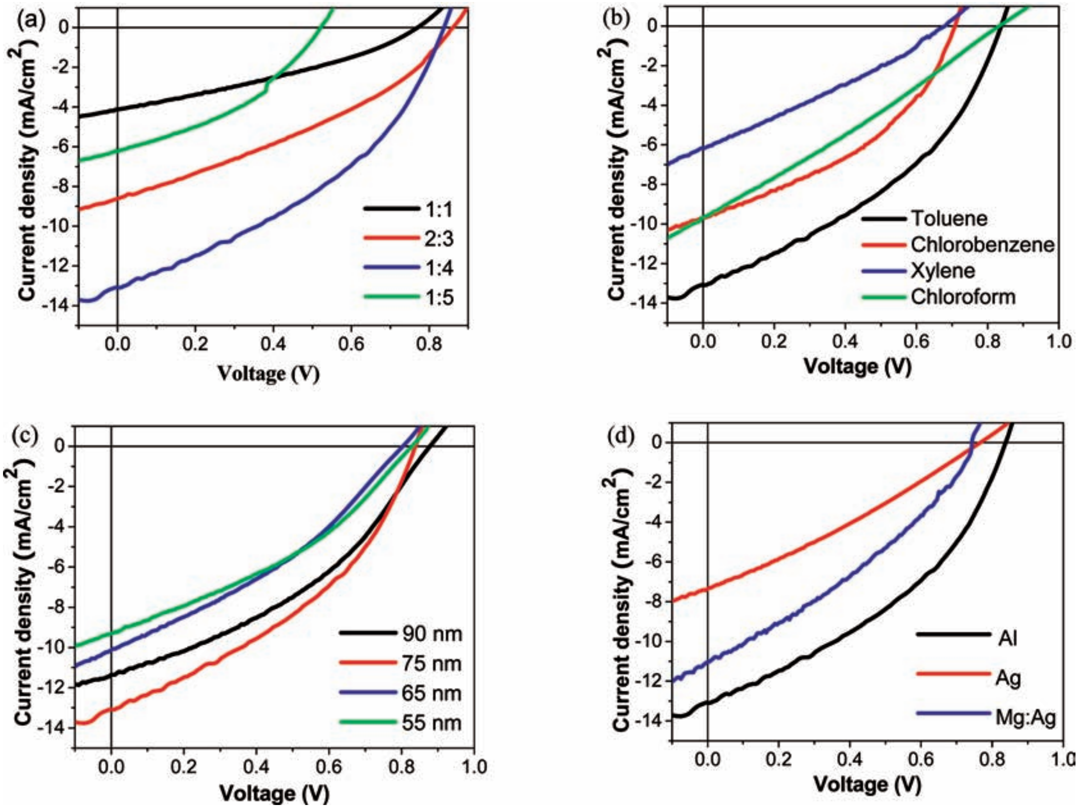


FIGURE 13. Dependence of the *J*−*V* curves of **1**/PCBM blend solar cells under different fabrication conditions.

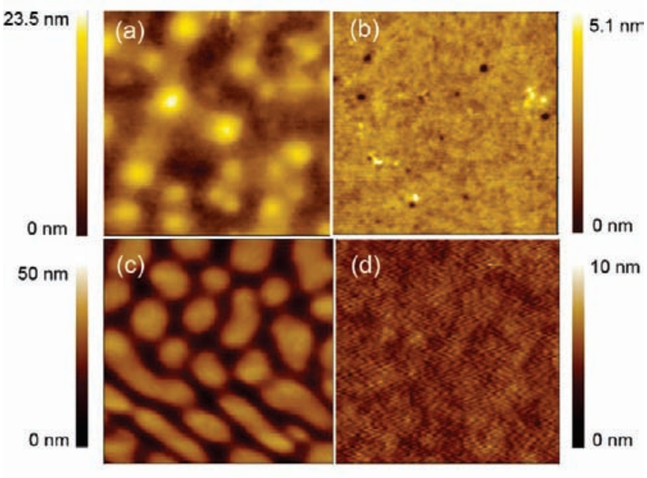


FIGURE 14.

FIGURE 14. AFM topography images of blend films: (a) **1**/PCBM (1:4), (b) **1**/PCBM (1:1), (c) **8**/PCBM (1:4), and (d) **8**/PCBM (1:5).

mal morphology of a blend film should provide a large interface for efficient exciton dissociation and, at the same time, sufficiently large phase-separated domains for free charge transport to the appropriate electrodes. The morphological requirement for the photoactive layer in a high-efficiency PSC is nanoscale phase separation, with the dimensions of D−A interface within the exciton diffusion length (typically on the order of 10 nm for conjugated polymers).[29] In organometallic systems, blend-ratio dependence on morphology and phase separation was also observed. From atomic force microscopy (AFM) images of blend films cast from toluene (Figure 14), significant phase separation occurs for a 1:4 blend ratio (∼20 nm) with no apparent formation of larger PCBM domains, while films with a 1:1 ratio are smooth (∼3−5 nm).[18a] This small-scale phase separation facilitates exciton dissociation and charge transport, resulting in the reduction of recombination losses and an increase in J_{sc}.[29] Moreover, thermal annealing of many of the polymers (e.g., **1**) does not ameliorate the cell performance due to their amorphous nature, which is less sensitive to postprocessing compared with polycrystalline polymers.[18i] Interestingly, the dependence of cell performance on MW should not be overlooked because MW and polydispersity variations can cause significant changes in the degree of crystallinity and blend morphology.[30] While our preliminary studies on amorphous polymer **1** indicated a strong dependence of morphology and PCE on MW, which resulted in a discrepancy among the efficiency data reported by different groups,[18a,i,26,31] further investigations on this issue are deemed necessary.

Overall, polymer properties and film preparation should both be optimized to give a desirable morphology exhibiting phase separation on a small scale, which represents a com-

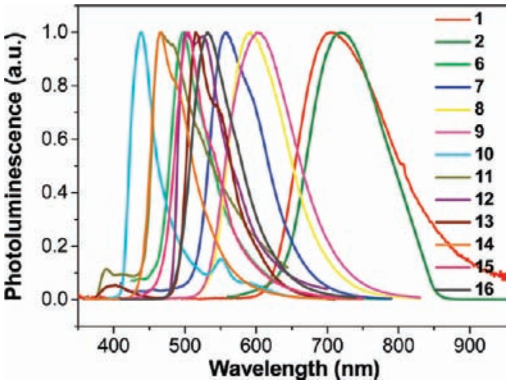
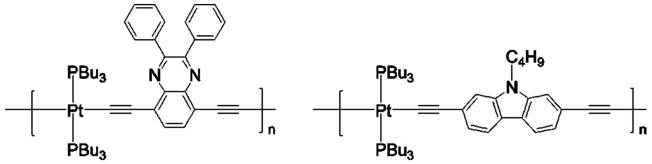


FIGURE 15. Emission color tunability for polyplatinynes.



35 **36**

FIGURE 16. Two examples of polyplatinynes used in PLEDs.

promise between exciton dissociation and charge collection, while surface roughness features with about 1 order of magnitude larger lateral size are formed simultaneously to improve light-trapping and charge collection.

5. Other Applications in Organic Photonics and Electronics

5.1. Polymer Light-Emitting Diodes (PLEDs). While solar cells use sunlight to produce electricity, another stream of current research focuses on the reverse of this process, that is, using electricity to produce light as in light-emitting diodes. Organometallic polyynes were investigated for both of these energy transformations. PLEDs are more energy-efficient and generally lower in cost than liquid-crystal displays.

From Figure 15, the emission wavelength of Pt polyyne can scan from blue (439 nm) to NIR (716 nm) by change of the central spacer, rendering their potential for full-color light emission. Realization of PLEDs using Pt polyynes (e.g., **6**, **10**, **35**, and **36**) as the emissive layer was nicely demonstrated (Figures 16 and 17).[32] Green electrofluorescence was observed for **6**, whereas intense green-yellow electrophosphorescence was obtained for **36**. For **10** and **35**, dual emission peaks from both singlet and triplet states were noted. The CIE coordinates at (0.357, 0.357) for **10**-doped PLED even approach a near-white emission. The efficiency of the diode is much higher for **36** (4.7 cd/A) than **6** (0.11 cd/A).[32a,b]

Here, clear distinction must be pointed out between PSCs and PLEDs. The presence of a heavy atom increases the intersystem crossing rate, and the lowest-energy triplet-state is prone to be largely populated relative to the singlet-state homologue in organic systems. This is favorable for PLED applications because energy from both singlet and triplet states can be harvested. However, the increase in triplet-state population implies a decrease in singlet-state ones, and the probability of electron transfer in the less populated singlet is smaller. These make potential PSC applications less plausible.

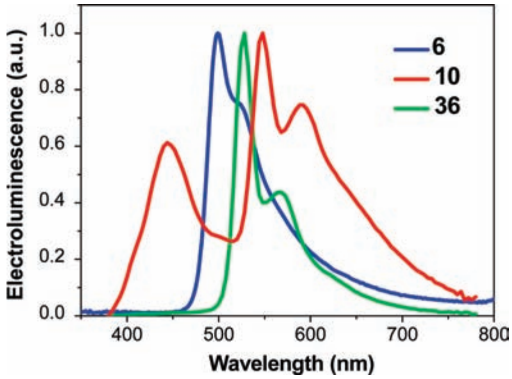


FIGURE 17. Electroluminescence spectra of **6**, **10**, and **36**.

5.2. Organic Field-Effect Transistors (OFETs). Recently, interest in OFETs has grown dramatically because of their potential applications in active-matrix back planes for flexible displays, sensors, and low-cost memory devices.[33] Soluble π-conjugated organometallic polymers have shown great promise in OFETs. In the proof-of-concept experiments, the semiconducting properties of **1** and **3**–**5** were first demonstrated by measuring their mobilities using an OFET configuration (Figure 18).[18i] The OFET capabilities of **20**, **21**, **23**, **26**, **27**, and **29**–**31** were also reported.[18h] We observed *p*-channel characteristics in all cases. Compared with **1**, the μ_h and on/off ratio significantly improved from 6.1×10^{-5} cm^2/(V s) and $\sim 10^2$ to 1.5×10^{-3} cm^2/(V s) and $\sim 10^4$ in **3**. By use of the rigid spacer in **5** to enhance the electron coupling between the D and A units, μ_h improved to 0.01 cm^2/(V s) with very high current modulation of $>10^6$. Electron transport was, however, not observed so far.

6. Conclusions and Future Perspectives

Organic materials have already transformed display technology and could soon challenge traditional inorganic photovoltaics for specific applications. The dynamic field of organic photovoltaics is gaining momentum through continued breakthroughs in materials and device performances. Though still in its infancy, combining metallic elements with polymers in metallopolymers should bring about the best of both worlds. Organometallic photovoltaics based on Pt–poly(arylene ethynylene)s spawned an area of current research and have ample applications as converters for light/electricity signals. Research-

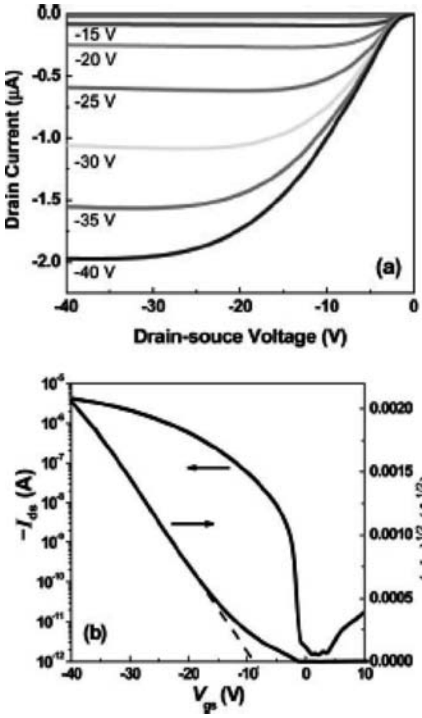


FIGURE 18. (a) Output and (b) transfer characteristics of OFETs fabricated from **5**.[18i]

ers are currently using platinum, though the research may later be extended to other metals. They are grappling with how to increase the efficiency of the devices and ensure that they can withstand wear and tear. Despite all these recent contributions, many aspects of metallopolyyne solar cells are still unexplored, and vast opportunities remain and many discoveries remain to be made. The concept to design polymers involving triplet states in charge generation could also become interesting for a next-generation PSC material. The uses of diblock metallo-copolymers and two semiconductors with different bandgaps (e.g., for tandem cells or all-polymer cells) would also warrant future examination. Here, it may be possible to utilize porphyrin-based polymers for photovoltaic applications, in which the Soret and Q-bands would secure the light harvesting between 400−450 and 600−650 nm and another metallopolyyne can cover the missing region (450−600 nm). To date, the killing problem in these cells is the low FF. We expect FF to improve for fabrication and characterization to be done under inert gas encapsulation to avoid the presence of traps. Further refinement on the device efficiency and lifetime is needed to make more practical devices.

The United Nations declared 2011 as the International Year of Chemistry. Chemistry will definitely continue to make important contributions to the global energy problem. The innovative design of new functional metallopolymers is very useful in energy-producing (solar cells) and energy-saving (PLEDs) applications, and we look forward to these exciting developments with substantial optimism.

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FOOTNOTES

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