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High performance small molecule photodetector with broad spectral response range from 200 to 900 nm

Shuang-hong Wu,[1,2] Wen-lian Li,[1,a)] Bei Chu,[1,a)] Zi-sheng Su,[1] Feng Zhang,[4] and C. S. Lee[3,a)]

[1]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China*
[2]*Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China*
[3]*Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Hong Kong SAR, People's Republic of China*
[4]*Key Laboratory of Optical System Advanced Manufacturing Technology, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China*

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We demonstrate a photodetector (PD) with broad spectral response by taking the advantages of more flexible device design in using small molecule materials. The optimized device shows an external quantum efficiency of over 20% from 200 to 900 nm. The high performance is achieved by jointing two donor (D)/acceptor (A) hetero-junctions [m-MTDATA(D)/TiOPc(A) and TiOPc(D)/F_{16}CuPc: PTCDI-C8(A)] such that photoresponses over the deep-ultraviolet (UV) and visible-near infrared regions can be independently optimized. By choosing D- and A-materials with matched energy level alignment, high carrier mobility, and balanced carrier transporting properties, the present PD shows a fast response of 56 ns. The high speed and deep-UV sensitivity might lead to potential military applications such as missile tracking in addition to optical communications, chemical/biological sensing etc. © *2011 American Institute of Physics*. [doi:10.1063/1.3610993]

Organic ultraviolet (UV)-visible and near infrared (NIR) photodetectors (PDs) have recently attracted much attention for their advantages including large-area detection, low-cost fabrication, and potential flexiblility.[1–6] In contrast, inorganic counterparts such as GaN-, Si-, and InGaAs-based PDs are being used for three important sub-bands, 250 to 400 nm (UV), 450 to 800 nm (visible), and 900 to 1700 nm (NIR), respectively. The recent work of Gong *et al*. made an important breakthrough in polymeric PD in terms of spectral response range.[7] By using an active layer of a small-band-gap π-conjugated polymer blended with a fullerene derivative, their PD gives a very wide spectral response from 300 to 1450 nm with a detectivity larger than 10^{12} Jones. However, there is so far no report on small molecule materials PDs with photoresponse spanning from deep UV to NIR region. Small molecule devices have the advantages of allowing flexible multilayer structures with no need of considering mutual solubility issues in multilayer polymeric devices. This implies that a wider range of materials can be selected and matched for optimizing the electronics and optical properties.[8]

In this work, we use a multilayer structure in which oxotitanium phthalocyanine (TiOPc) is sandwiched between materials with respectively strong electron donating and accepting properties. TiOPc has a molecular structure similar to that of copper-phthalocyanine (CuPc) and is expected to have similar bipolar properties.[9] We have observed that device with a bilayer structure of m-MTDATA/TiOPc can give good photovoltaic (PV) response under UV illumination, confirming the electron-accepting properties of TiOPc, which will be reported elsewhere. Thus, TiOPc would form two connected donor/acceptor hetero-junctions, which can be optimized for PD responses over the deep-UV and visible-NIR regions, respectively. The performance is further enhanced by using an ohmic contact anode of ITO/m-MTDATA and a cathode buffer layer of Cs_2CO_3 doped BPhen for efficient charge collection. The optimized device shows a good spectral response from 200 to 900 nm with a high quantum efficiency of over 20% and a fast response time of 56 ns.

All chemicals were purchased commercially and used without further purification. Organics and metal layers were sequentially deposited onto the clean patterned ITO glass substrates with a sheet resistance of 25 Ω/sq via shadow masks to form devices with an area of 0.03 cm^2. Deposition rates and thickness of all layers were monitored in *situ* using an oscillating quartz monitor. Absorption spectra of the organic films on quartz substrates were measured with a Shimadzu UV-3101PC spectrophotometer. Current-voltage (I-V) characteristics were measured with a semiconductor parameter analyzer (Keithely 2400) in dark and under illumination of $\lambda = 800$ nm. External quantum efficiency (EQE) was measured in a SPEX scanning monochromator with a 150 W Xe lamp as the illumination source from the cathode side. Response speeds of the devices were measured under an irradiation of a 808 nm laser with a pulse width of 60 ns and a repetition rate of 1 kHz. The transient voltage across a 50 Ω load was recorded using a 100 MHz bandwidth oscilloscope. All measurements were performed under ambient conditions with unpackaged devices.

Fig. 1 shows absorption spectra of 30 nm thick pristine films of CuPc, TiOPc, N,N′-Dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8), and hexadecafluoro-copper-phthalocyanine (F_{16}CuPc) on quartz substrates, respectively. The materials are selected such that their optical absorptions cover a broad spectral region from 200 nm to 900 nm. Four

a)Authors to whom correspondence should be addressed. Electronic addresses: wllioel@yahoo.com.cn, beichu@163.com, and apcslee@cityu.edu.hk.

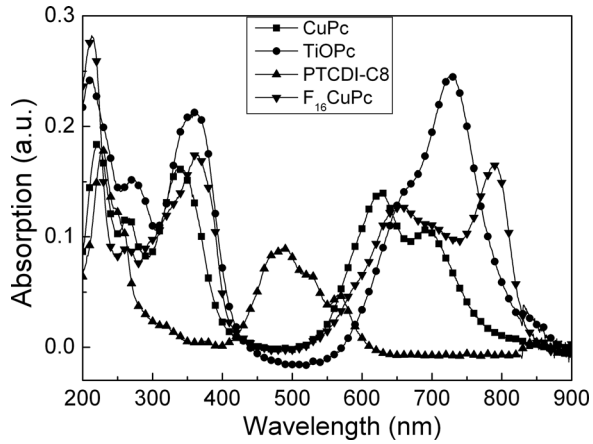

FIG. 1. Absorption spectra of 30 nm thick pristine films of CuPc, TiOPc, PTCDI-C8, and F_{16}CuPc on quartz substrates.

devices were fabricated with a structure of ITO anode/organic layers/Cs_2CO_3:BPhen (30 wt. %, 10 nm) buffer layer/Al (12 nm)/Ag (20 nm) cathode. The organic layers used in the four devices are

Device A: m-MTDATA (10 nm)/CuPc (20 nm)/PTCDI-C8 (40 nm),

Device B: m-MTDATA (10 nm)/CuPc (20 nm)/F_{16}CuPc: PTCDI-C8 (1:1, 40 nm),

Device C: m-MTDATA (10 nm)/TiOPc (20 nm)/F_{16}CuPc: PTCDI-C8 (1:1, 40 nm), and

Device D: TiOPc (20 nm)/F_{16}CuPc: PTCDI-C8 (1:1, 40 nm).

Devices A to C have a trilayer structure in which a bipolar material (CuPc or TiOPc) is sandwiched between strong electron donor and acceptor, considered as two jointed donor/acceptor junctions. Schematic energy level diagrams of devices A, B, and C are shown in Fig. 2(a), in which the LUMO and HOMO data were cited from Refs. 10–13 for m-MTDATA, CuPc, TiOPc, and F_{16}CuPc as well those of PTCDI-C8 were determined by cyclic voltammetry,[14] respectively. The energy level of F_{16}CuPc is shown in dotted line.

Devices A and B have acceptor layers of PTCDI-C8 and F_{16}CuPc: PTCDI-C8, respectively. The mixed layer used in device B is intended for extending the PD response range by making use of the complimentary absorption spectra of the two components. Device C uses TiOPc instead of CuPc as the bipolar material to exploit the better absorption of TiOPc over the range of 600–800 nm and its better donor performance.[15] Device D is a control device used for studying the effects of the m-MTDATA layer.

EQEs of the four devices are shown in Fig. 2(b). Device A has a lower EQE over 700–900 nm in comparison with others due to the lack of NIR absorption from F_{16}CuPc (Fig. 1). However, it shows that Device A has higher efficiency than Device B at the wavelength before 700 nm, which may be the result of charge mobility change arised by the blend acceptor layer. Device C shows higher EQEs across the entire spectral range comparing to Device B and higher EQEs than Device A over the NIR region, which is over 20% from 200 nm to 900 nm abroad wavelengths. It should also be pointed out that EQEs of the detectors are higher than 100% over the UV region. Such EQEs larger than unity have been reported in many organic PDs.[16–20] The mechanisms for such photomultiplication (PM) effects have been studied systematically by Huang *et al.*[16] They pointed out that due to the large exciton binding energy of organic materials, the PM should not be due to impact ionization as in inorganic semiconductors. They further showed that release of carriers from interfacial traps is the dominant mechanism in their system. In the present photodetectors, there are many more interfaces, which might lead to the PM effects. However, relative contributions from individual interfaces are still not clear and further studies would be needed to clarify the PM mechanisms.

Fig. 3 shows the relation of the photocurrent/dark current densities versus bias voltage of Device C under 800 nm illumination with an intensity of 1.12 mW/cm^2. The photoresponsivity R was determined using the following Eq. (1)

$$R = \frac{J_p - J_d}{P_o} \tag{1}$$

where P_0 is the incident light intensity, J_p and J_d are respectively the photo- and the dark-current densities at a certain reverse biases. At a bias of −3 V, Device C gives a photocurrent of 305.4 μA/cm^2 and a dark current of 0.31 μA/cm^2, respectively. These give a responsivity of 0.27 A/W, which is 60% higher than that of the polymer PD reported by Gong *et al.*[7] The specific detectivity can be expressed as $D^* = R/(2qJ_d)^{1/2}$, where q is the electron charge (1.6×10^{-19} Coulombs). Device C gives a specific detectivity of about 1×10^{12} Jones at − 3 V. In addition to sensitivity, fast response is also an important requirement for high-speed applications. The response speed of Device C at − 3 V was measured with a

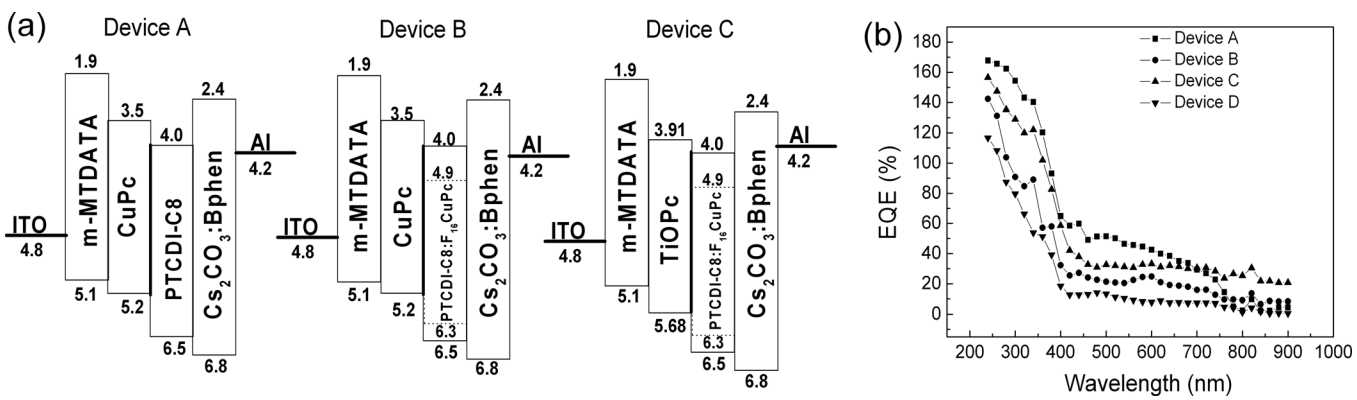

FIG. 2. (a) Schematic energy level diagrams of Devices A, B, and C. (b) EQE of the four devices at −3 V.

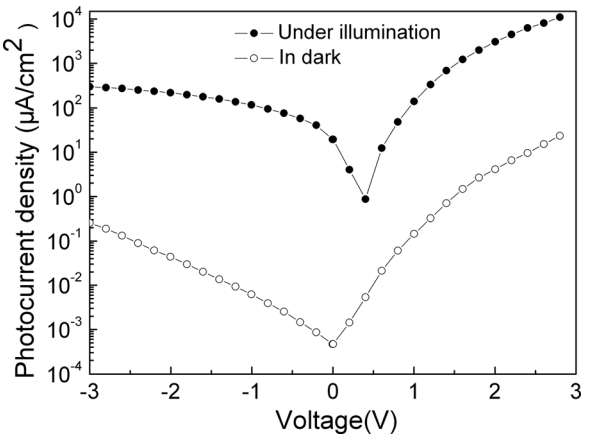

FIG. 3. Current density-voltage (J-V) characteristics of Device C under 800 nm illumination with an intensity of 1.12 mW/cm^2.

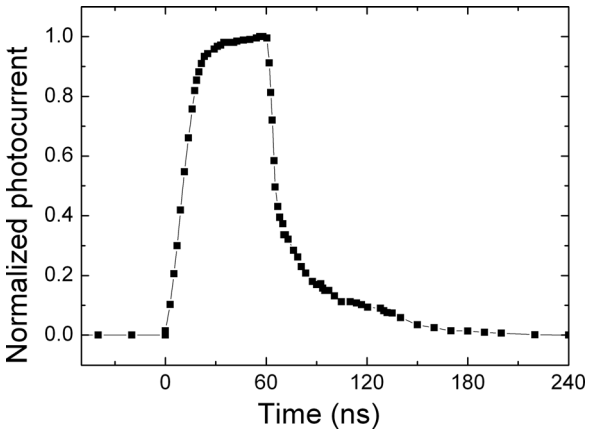

FIG. 4. Electrical response of Device C at −3 V with $\lambda = 808$ nm emission from a laser with a pulse width of 60 ns and a repetition rate of 1 kHz.

808 nm pulsed laser (pulse width = 60 ns) and a load resistance of 50 Ω, as shown in Fig. 4. A 90%-10% fall time of about 56 ns was obtained, which can satisfy the demand of high-speed response.

In order to understand the importance of m-MTDATA in the PDs, we compared the performance of Devices C and D. It can be seen from Fig. 2(b) that the EQE of Device C is higher than that of Device D over the entire spectral range. m-MTDATA is considered also to play another two roles besides the above-mentioned electron-donor function in Device C. Firstly, it forms an ohmic contact with ITO for hole collection,[10] and secondly it also plays the role of an electron blocking layer, as shown in Fig. 2(a). The LUMO difference of 2 eV at the m-MTDATA/TiOPc interface is expected to efficiently block the photo-generated free electron from going to the anode side.

As mentioned above the mixed F_{16}CuPc: PTCDI-C8 layer acts as an electron-acceptor. PTCDI-C8 is a perylene derivative and has been used as an electron acceptor in PV devices and thin-film transistors due to its very high electron mobility of 0.6 cm^2 V^{-1}s^{-1}.[21,22] On the other hand, F_{16}CuPc has a high electron-mobility of 10^{-4} cm^{2}V^{-1}s^{-1} (determined in-house by time-of-flight measurement). The PTCDI-C8:F_{16}CuPc mixed acceptor layer is thus expected to have good electron-transporting properties. In addition, they have complementary optical absorption spectra as shown in Fig. 1. Indeed, the devices (B, C, and D) with F_{16}CuPc do give better PD spectra response than the device (A) without it over the NIR region (Fig. 2(b)). BPhen doped with Cs_2CO_3 is used as a cathode buffer layer which plays an important role in achieving high EQE by forming an ohmic contact at the cathode side. The uses of m-MTDATA and Cs_2CO_3 doped BPhen also are important for a balanced carrier collection at the two electrodes.[23]

In conclusion, high performance photodiodes using small molecule materials with wide spectral response from 200–900 nm were demonstrated. The optimized photodiode shows EQE of higher than 20% over the entire response range, a detectivity of ~10^{12} Jones and a fast response time of 56 ns. The high PD performance is attributed to careful selection of materials with complimentary absorption spectra, matched energy levels, and use of electrodes with high charge collection efficiency.

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[1]G. Yu, J. Wang, J. McElvain, and A. J. Heeger, Adv. Mater. **10**, 1431 (1998).
[2]D. Ray and K. L. Narasimhan, Appl. Phys. Lett. **91**, 093516 (2007).
[3]P. Peumans, V. Bulovic, and S. R. Forrest, Appl. Phys. Lett. **76**, 3855 (2000).
[4]Y. Yao, Y. Y. Liang, V. Shrotriya, S. Q. Xiao, L. P. Yu, and Y. Yang, Adv. Mater. **19**, 3979 (2007).
[5]M. Binda, T. Agostinelli, M. Caironi, D. Natali, M. Sampietro, L. Beverina, R. Ruffo, and F. Silvestri, Org. Electron. **10**, 1314 (2009).
[6]M. Liao, Y. Koide, and J. Alvarez, Appl. Phys. Lett. **90**, 123507 (2007).
[7]X. Gong, M. H. Tong, Y. J. Xia, W. Z. Cai, J. S. Moon, Y. Cao, G. Yu, C.-L. Shieh, B. Nilsson, and A. J. Heeger, Science **325**, 1665 (2009).
[8]S. R. Forrest, Nature (London) **428**, 911 (2004).
[9]L. L. Chen, W. L. Li, H. Z. Wei, B. Chu, and B. Li, Sol. Energy Mater. Sol. Cells **90**, 1788 (2006).
[10]C. Giebeler, H. Antoniadis, D. D. C. Bradley, and Y. Shirota, Appl. Phys. Lett. **72**, 2448 (1998).
[11]G. Zhang, W. L. Li, B. Chu, L. L. Chen, F. Yan, J. Z. Zhu, Y. R. Chen, and C. S. Lee, Appl. Phys. Lett. **94**, 143302 (2009).
[12]J. Ye, H. Z. Chen, and M. Wang, Mater. Chem. Phys. **82**, 210 (2003).
[13]T. Sakanoue, T. Irie, and C. Adachi, J. Appl. Phys. **105**, 114502 (2009).
[14]H. Wang, B. S. Xu, X. G. Liu, H. F. Zhou, Y. Y. Hao, H. X. Xu, and L. Q. Chen, Org. Electron. **10**, 918 (2009).
[15]M. Brumbach, D. Placencia, and N. R. Armstrong, J. Phys. Chem. C **112**, 3142 (2008).
[16]J. Huang and Y. Yang, Appl. Phys. Lett. **91**, 203505 (2007).
[17]W. T. Hammond and J. Xue, Appl. Phys. Lett. **97**, 073302 (2010).
[18]J. Gao and F. A. Hegmann, Appl. Phys. Lett. **93**, 223306 (2008).
[19]F.-C. Chen, S.-C. Chien, and G.-L. Cious, Appl. Phys. Lett. **97**, 103301 (2010).
[20]I. H. Campbell and B. K. Crone, J. Appl. Phys. **101**, 024502 (2007).
[21]S. Karak, S. K. Ray, and A. Dhar, Sol. Energy Mater. Sol. Cells **94**, 836 (2010).
[22]P. R. L. Malenfant, C. D. Dimitrakopoulos, J. D. Gelorme, L. L. Kosbar, T. O. Graham, A. Curioni, and W. Andreoni, Appl. Phys. Lett. **80**, 2517 (2002).
[23]S. H. Wu, W. L. Li, B. Chu, C. S. Lee, Z. S. Su, J. B. Wang, F. Yan, G. Zhang, Z. Z. Hu, and Z. Q. Zhang, Appl. Phys. Lett. **96**, 093302 (2010).