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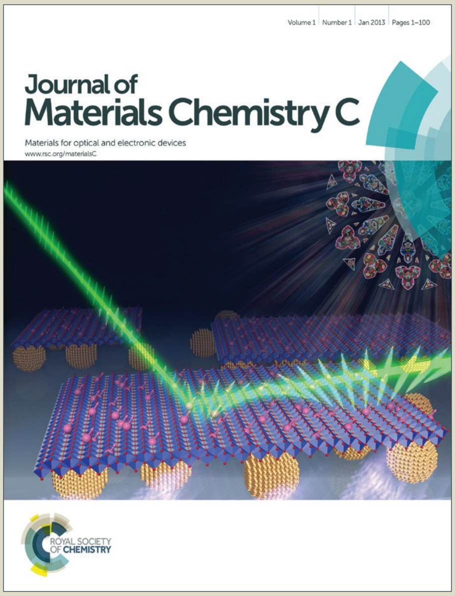

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Synthesis and Application of Benzooxadiazole Based Conjugated Polymers in High Performance Phototransistors

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Four planar conjugated polymers named **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** with carbazole as the donor unit and benzooxadiazole or benzothiadiazole as the acceptor unit have been synthesized and characterized. These four polymers are of medium band gaps (1.95 - 1.97 eV), low-lying HOMO energy levels (below -5.5eV), relatively high hole mobilities (in the range of 0.026 - 0.1 $cm^2 V^{-1} s^{-1}$), and on/off current ratio of 10^6 without any post-treatment. Moreover, high performance thin film phototransistors based on these four polymers have also been fabricated with high photocurrent/dark current ratios (5.7×10^3 - 8.2×10^3). Interestingly, phototransistors based on **CZ-BO8** and **CZ-BO12** show faster photoresponse than that based on **CZ-BT8** and **CZ-BT12**, providing valuable molecular design guideline for high performance photoresponse polymers.

Introduction

Among optoelectronic devices, phototransistor that is a kind of three terminal device with photo as the ‘‘fourth terminal’’ have been attested to be extraordinary effective in combining light detection and signal magnification properties together to achieve the functionalities in a single device.[1,2,3-6] Critical processes that limit the high-performance realization of phototransistors include the generation of charge carriers under light irradiation, the transfer of charge carriers, and the collection of charge carriers for signal magnification.[7–13] Since the gate applied bias provides a valid way for the dissociation of the photo generated excitons into free charge carriers and is also beneficial for the charge carrier transport and collection,[14] phototransistors exhibit high efficiency for the above mentioned processes and can achieve effective photo detection. Since William Shockley discovered the phototransistor,[15-18] inorganic semiconductor-based phototransistors are well developed and used widely in our daily life, such as in optoisolators, highly sensitive optical switches and retro sensors etc. However, phototransistors fabricated with conjugated polymers[19-21] whichhave been considered as a class of solution processable and cost-effective semiconductors due to their attractive superiorities in mechanical flexibility, optical and electronic properties be tuned by chemical modification,[22-29] are not widely used.

The challenges we face for the application of conjugated polymers in phototransistors are how to efficiently generate, transport and collect charge carriers. The narrow absorption band of most conjugated polymers limits the generation of charge carriers and the low mobility of most conjugated polymers limits the efficiency of charge carrier transportation and collection, leading to the low performance of conjugated polymer based phototransistors. So, on the one hand, for efficient chargecarrier generation the donor (D)–acceptor (A) structure is widely used in synthetic design of conjugated polymers with narrow band gap to harvest more incident photons.[30-33] On the other hand, the low mobility of conjugated polymers is a result of their non-planar structures, which are detrimental for the close packing of polymer chains in the solid state and retard the intermolecular charge carrier hopping and transporting.It is vital to design and synthesize polymers that can pack closely in the solid state and also have good solution processability. Our synthetic strategies were inspired by our early work on planar conjugated polymers.[7,34] Here we choose the widely used benzothiadiazole and benzooxadiazole as the acceptor units for the synthesis of D–A alternating conjugated polymers for high-efficiency photoconducting devices. With these acceptors, we select another planar carbazole as the donor unit. Four planar D-A conjugated polymers(as shown in Scheme 1) named **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** are designed, with two octyloxy (or dodecyl) chains on the benzothiadiazole (or benzooxadiazole), a 2-hexyldecyl chain on the carbazole, and two flanked thiophene units as the spacer. The flexible alkyl chains make these polymers soluble in organic solvent at elevated temperature, and the polymer chain could have a planar conformation to facilitate charge carrier transport for photoconducting applications. The structures of four soluble

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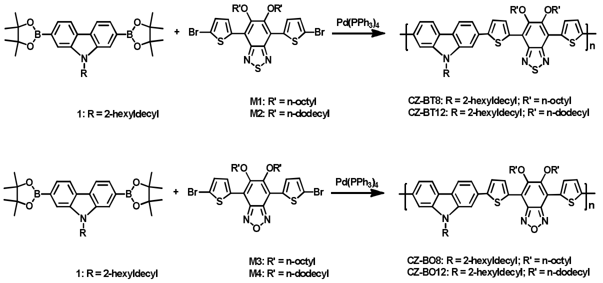
Electronic Supplementary Information (ESI) available: Experimental part includingSynthesis of four polymers, Field-effect transistor fabrication, AFM spectra, and ^{1}H NMRspectraof polymers.

polymers were fully characterized, and their optical, electrochemical, and photovoltaic properties were investigated in detail to explore their structure and property relationships.

Results and discussion



Scheme 1.Synthesis of polymers.

Material Synthesis and Characterization

The synthesis of polymers **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** is outlined in Scheme 1. Polymerization of carbazole based dibromo monomer and benzothiadiazole or benzooxadiazole based diboronic acid pinacol ester monomer under standard Suzuki polycondensation conditions afforded these four polymers. All these four polymers are insoluble at common organic solvents such as chloroform, chlorobenzene (CB), and 1,2-dichlorobenzene (DCB) at room temperature, but can be fully dissolved in DCB and 1,2,4-trichlorobenzene (TCB) at elevated temperature. The molecular weights and molecular weight distributions of these four polymers were measured by gel permeation chromatography (GPC) at 150 ˚C using TCB as an eluent and narrowly distributed polystyrenes as the calibration standards, and the results are summarized in Table 1. It is worth noting that we have obtained high molecular weight materials. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to investigate the thermal properties of these four polymers. Under nitrogen atmosphere at a heating rate of 10 °C/Min, all the four polymers exhibited good thermal stability with the 5% decomposition temperature up to 312 °C for **CZ-BO8**, 307°C for **CZ-BO12**, 324 °C for **CZ-BT8**, and 321 °C for **CZ-BT12**. The results are also summarized in Table 1. DSC measurements under nitrogen atmosphere at a heating rate of 20 °C/Min in the range of 20 to 300 °C showed that there was no obvious glass transition for all the four polymers. Powdery XRD measurement as shown in Fig.2 was used to investigate the packing of polymer chains in the solid state. All these polymers showed one diffraction peak at small angle region, which reveals the distance of polymer chains separated by the flexible chains, and one broad diffraction peak at wide angle region, which reflects the π–π stacking distances between polymer chains. The diffraction peakintensityof**CZ-BO8** and **CZ-BO12** at wide angle region isobviously higher thanthat of **CZ-BT8** and **CZ-BT12**, demonstrating that **CZ-BO8** and **CZ-BO12**have better crystallinity.The detailed XRD results are summarized in Table 2.

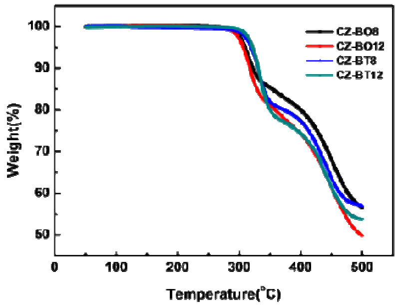


Fig.1 TGA of polymers.

Table 1. Physical properties of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12**.

Polymer	M_n(kg/mol) [a]	M_w(kg/mol) [a]	PDI	T_d (°C) [b]
CZ-BO8	13.4	44.0	3.28	312
CZ-BO12	18.9	65.7	3.48	307
CZ-BT8	17.7	47.7	2.69	324
CZ-BT12	19.6	56.3	2.87	321

[a] M_n, M_w, and PDI were determined by GPC at 150 °C using polystyrene as the calibration standards as TCB as the eluent.

[b] Decomposition temperatures were determined by TGA under N_2 based on 5% weight loss.

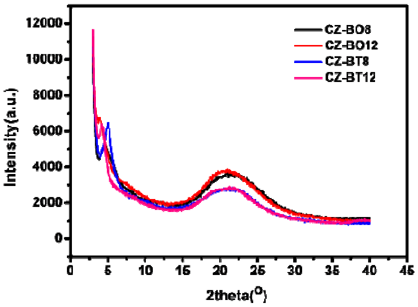


Fig.2 Powdery XRD patterns of polymers.

Table 2. The packing of polymer chains in the solid state.

Polymer	2θ (°)[a]	distance (Å) [b]	2θ (°)[c]	distance (Å) [d]
CZ-BO8	4.63	19.31	21.45	4.19
CZ-BO12	3.84	23.28	20.94	4.29
CZ-BT8	5.02	17.81	21.07	4.26
CZ-BT12	4.23	21.14	20.80	4.32

[a] 2θ was the first peak in the small angle region of the XRD diffraction patterns.

[b] The distance was that polymer backbones separated by the flexible side chains.

[c] 2θwas the broad diffraction peaks in the wide angle region.

[d] The distancewas π-π stacking distances between polymer backbones

Optical Properties

UV–vis absorption spectra of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** in DCB solutions and as thin films are shown in Fig.3. To eliminate the influence of polymer chain aggregation in solution at room temperature, the UV–vis absorption spectra of polymer solutions were therefore measured at 100 °C. Both in solutions and as thin films, all the four polymers exhibited two absorption peaks, and their locations are summarized in Table 3. Compared with their solution absorption spectra, the obvious difference is that the corresponding film ones were red-shifted with a distinct shoulder due to the aggregation of polymer chains in the solid state. The relatively wide absorption range of these polymers suggested the transition from its highest occupied molecular orbital (HOMO) to its lowest unoccupied molecular orbital (LUMO) is very easy, indicating that they are easily excited by light.The film absorption onsets (λ_{edge}) of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** are 636, 634, 634 and 631 nm, respectively. Increasing the volume of substituent group on the benzothiadiazole moiety could increase the π–π stacking distance between polymer chains in the solid state and resulted in a blue-shift of the absorption peak. The optical band gaps ($E_{g,opt}$) of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** films were therefore calculated to be 1.95, 1.96, 1,96 and 1.97 eV, respectively, according to the equation: $E_{g,opt}$ = 1240/absorption onset. The medium band gap indicated that these four polymers could be easily excited by visible light.[35] So the series of BO and BT based polymers are good candidates for photo-controlled devices.

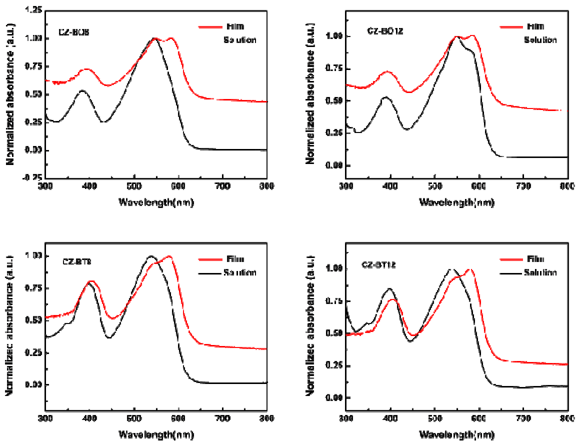


Fig.3UV-vis absorption spectra of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** in DCB solutions at 100 °C and as thin films.

Table.3 Electrochemical and optical properties of polymers.

Polymer	λ_{max}(nm) solution	λ_{max}(nm) film	$E_{g,\ opt}$ (eV) [b]	HOMO (eV)	LUMO (opt, eV)[c]
CZ-BO8	383, 544	393, 583	1.95	-5.51	-3.56
CZ-BO12	388, 548	395, 585	1.96	-5.51	-3.55
CZ-BT8	398, 538	407, 579	1.96	-5.62	-3.66
CZ-BT12	396, 538	405, 579	1.97	-5.64	-3.67

[a] Measured at 100 °C.

[b] Calculated from the absorption onset the polymer film, $E_{g,opt}$ = 1240/ λ_{edge}.

[c] Calculated by the equation $E_{LUMO} = E_{HOMO} + E_{g,opt.}$

Electrochemical Properties

Using a standard three electrodes electrochemical cell, electrochemical properties of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** were investigated by cyclic voltammetry (CV). As shown in Fig.4, these four polymers exhibited quasi-reversible redox processes. The onset oxidation potentials (E_{ox}) of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** are 0.80, 0.80, 0.91 and 0.93 V, respectively, versus Ag/AgCl reference electrode. HOMO levels of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** were determined, using the equation $E_{HOMO} = -e(E_{ox} + 4.71)$, to be -5.51, -5.51, -5.62 and -5.64 eV, respectively. LUMO levels of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** were therefore calculated according to the equation $E_{LUMO} = E_{HOMO} + E_{g,opt}$ to be -3.56, -3.55, -3.66 and -3.67 eV, respectively. The data are also summarized in Table 3. The above results indicated that the introduction of big volume sulphur atom can lower the HOMO energy level of polymers relative to oxygen atom. The changing of alkoxyl substituent group on the benzothiadiazole unit has a subtle influence on their electrochemical properties.

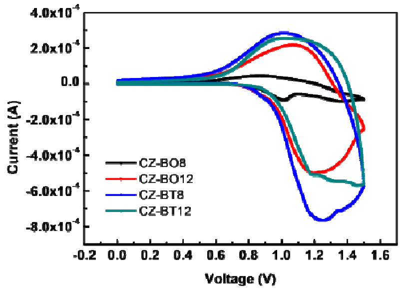
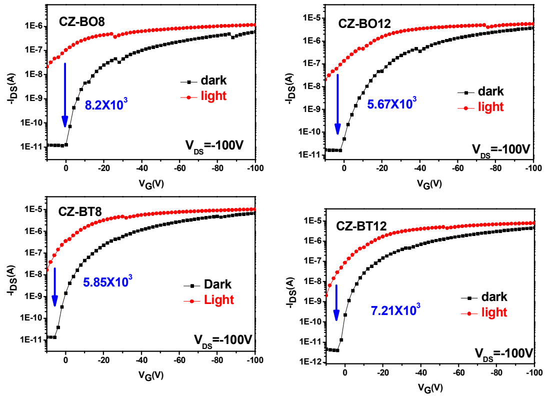


Fig.4 Cyclic voltammograms of polymers.

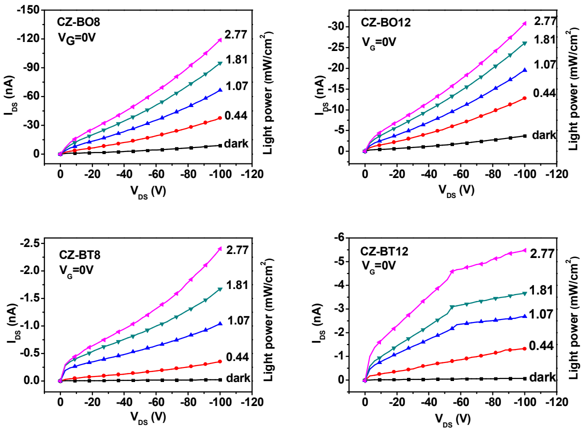
Field-effect transistor fabrication and characterization

Hole transport properties of polymers were investigated by fabrication of field-effect transistors (FETs). We fabricated top contact devices on Si/SiO_2 substrates with the low-resistance Si as gate and SiO_2 (500 nm) as gate insulator with a capacitance of 7.5 nF cm^{-2}. The substrate of Si/SiO_2 was sequentially cleaned with pure water, hot concentrated sulfuric acid-hydrogen peroxide solution (concentrated sulfuric acid: hydrogen peroxide (30%) = 2:1), pure water, pure 2-propanol, successively, then treated with trichloro(octadecyl)silane (OTS) by the normal vapor deposition method to form a monolayer on the surface of substrate. Polymer thin films were spin-coated or casted on the OTS modified Si/SiO_2 substrates from 1,2-dichlorobenzene (DCB) solutions. **CZ-BT8** and **CZ-BT12** were dissolved in DCB at 60 °C and **CZ-BO8** and **CZ-BO12** were dissolved in DCB at 110 °C. Au electrode (25 nm) was vacuum deposited on polymer thin films with width/length = 8 (where channel width = 0.24 mm, channel length = 0.03 μm). Current-voltage (I-V) characteristics were performed by a Keithley 4200 SCS with a Micromanipulator 6150 probe station in a clean and shielded box at room temperature under no light in air.The FET devices exhibited typical p-type behavior. The hole mobility (μ) was estimated in the saturated regime from the derivative plots of the square root of source-drain current (I_{SD})versus gate voltage (V_G)through the equation $I_{SD} = (W/2L)\ C_i\mu(V_G - V_T)^2$, where W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer (SiO_2, 500 nm, C_i= 7.5 nF cm^{-2}), and V_T is the threshold voltage. By 140 °C annealing tests for four polymer thin film devices, hole mobilities of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** reached 2.7×10^{-2}, 0.1, 4.0×10^{-2} and 2.6×10^{-2} cm^2 V^{-1}s^{-1}, and on/off ratios of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** were 2.4×10^6, 2.9×10^6, 2.5×10^6 and 2.0×10^6, respectively. The thin film morphology after annealing was investigated by atomic force microscopy (AFM) in tapping-mode. AFM images of the four polymer films are shown in the Fig. 8(vide infra).The transfer characteristic and output characteristic of OFET devices in darkness are shown in Fig. 5. No obvious contact resistance was observed in devices indicating an ideal energy level alignment between the HOMO level of polymers and the work function of Au source and drain electrodes.[36] The high hole mobility of **CZ-BO12** is probably attributed to its good crystallographic film morphology, which makes it facile to transport the effective free charge carriers.

(a)



(b)



(c)

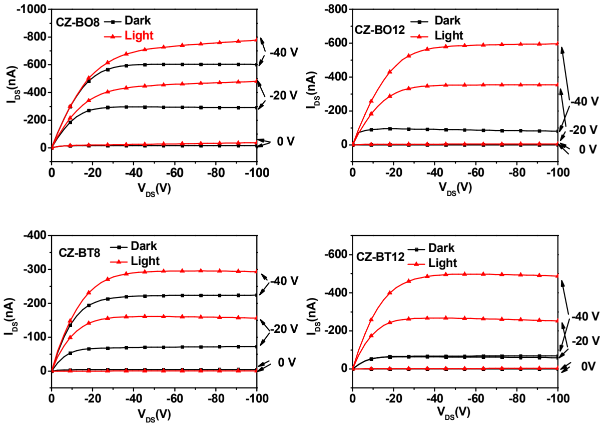


Fig.5(a) The transfer characteristics of devices fabricated with **CZ-BO8**, **CZ-BO12**, **CZ-BT8**, **CZ-BT12**in darkness and under the illumination of light with an intensity of 2.77 mW/cm^{2}at V_{DS} =-100 V. (b) The output characteristics of the transistors using light irradiation to substitute $V_G$with the light intensity changed from 0 to 2.77 mW/cm^2 with a fixed V_G=0V. (c) The output characteristics of devices at different $V_G$in darkness and under the illumination of light with an intensityof 2.77 mW/cm^2.

Phototransistors fabrication and characterization

Thin film phototransistors were fabricated with a deviceconfiguration similar to the field-effect transistors, but the devices from the side of polymer semi-conductor will be illuminated with the white light.With the irradiation of light, the devices exhibitedstrong photo dependences. Similar to organic field-effect transistors using V_G to control the source-drain current, the light could be used to substitute V_G as an independent variable to control the output of the transistors to realize light detection and signal magnification in a single organic device. The operational voltage of the phototransistors was very low (V_G = 0V, V_{DS} less than 10 V) and the sensitivity of the transistors to light was very high which indicate the potential applications of the devices for low power organic optoelectronics.

Typical photoresponse characteristics of the transistors are also shown in Fig.5. The ‘‘transfer’’ characteristics of the phototransistors in the dark and under illumination with a light intensity of 2.77mW.cm^{-2} are shown in Fig.5a. Owing to the contribution of the photocurrent, an obvious increase in the I_{SD} was observed under light illumination. The phototransistor maximum on/off ratio of **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12** were calculated to be 8.2×10^3, 5.7×10^3, 5.9×10^3 and 7.2×10^3 at V_G = 0 V, 2 V, 6 V, and 4 V, respectively. These on/off ratios are relatively high for conjugated polymer phototransistors, especially polymer thin film photoswitchers. Fig.5b displays the output characteristics of devices under illumination (2.77 mW/cm^2) and in dark at different gate voltages. We can observe a clear increase of drain current under illumination, indicating that the light illumination played an important role in tuning the properties of the transistors.

This conclusion can be further testified by the results of Fig.5c. Itis obvious that the incident light could be used to substitute the V_G as an independent variable to regulate and control the output characteristics of the transistors. In other words, the light could beused as the fourth terminal to optically control the device operation. The responsivity(R), an important parameter of phototransistors, can be defined as follows:[37]

$$R = \frac{I_{ph}}{P_{opt}} = \frac{(I_{DS,illum} - I_{DS,dark})S^{-1}}{P_{inc}}$$

whereI_{ph} is the source-drain photocurrent, P_{opt} is the incident light power, P_{inc} is the power of the incident light per unit area, $I_{DS,illum}$and $I_{DS,dark}$ are the drain-source current under illumination and in dark, respectively, and S is the effective area of the device. It is attractive that the R value of the phototransistors could reach 517, 665, 393 and 424 mA/W for **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12**, respectively, at a very low V_G. This value could be further improved by using a monochromatic light source with photon energy corresponding to the maximum absorption of the polymer.[38,39] As shown in Fig.5a, the high responsivity of transistors resulted in a large on/off ratio of optoelectronic devices.

The above results suggested that in an individual organic device the successful signal magnification and light detection can be achieved andalso demonstrated that these devices have potential applications in optoelectronic field such as highly sensitive optical switches, retrosensors, optoisolators, and so forth.[2]

These polymer devices also exhibited photoswitch characteristics too.[40] However, the highest switch ratio was below 1000, and the on/off ratio of the phototransistor are in the range of 5.67 × 10^3 to 8.2× 10^3 under 2.77 mW white light irradiation. It was obvious that the on/off ratio of the phototransistors was much higher than that of the two end devices. It probably put down to that the gate-applied bias of transistors made the photogenerated excitons dissociation more efficientand was also profitable for the production of

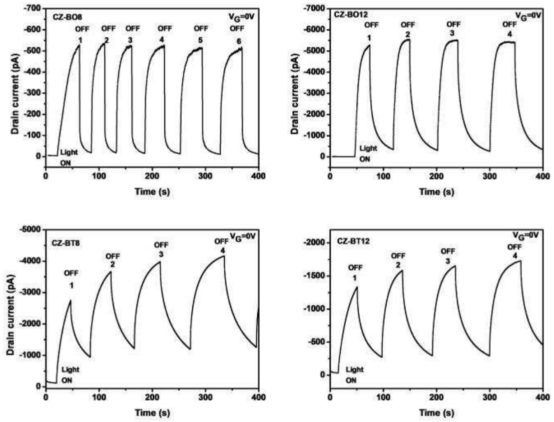


Fig.6 Photoswitch properties of four polymers with an applied gate bias of 0V at V_{DS}=-10V with a whitelight intensity of 2.77mW/cm^2.

Fig. 7shows the response time of photocurrent growth and decay for these four polymers in response to the white light being turned on and off. For comparison, the drain current of four devices were times to reach same level. The circles are experimental points and the solid lines are fitted according to the following equations. The dynamic response of our device to the light source can be well described by $I(t) = I_{dark} + A[\exp(t/\tau)]$ and $I(t) = I_{dark} + A[\exp(-t/\tau)]$ for growth and decay,[41,42] respectively, where τ is the time constant and t is the time when light was switched on or off, I_{dark} is the dark current, and A and B are scaling constants. From these fits, the growth time constants and the decay ones were estimated. The device current of **CZ-BO8**, **CZ-BO12** rises within 1 s when the illumination is turned on. The rapid photocurrent rise is followed by a slower component, in which the photocurrent increases with an estimated time constant of 6.3 s and 5.6 s, before saturating. But for **CZ-BT8** and **CZ-BT12**, they do not have a rapid process. During the course of the current going up, the time constant was about 17.1 s and 12.7 s, which is several times to the series of BO. After the excitation is turned off, photocurrent decay starts with a fast decay less in 1s. Subsequently, a slow photocurrent decay process lasts with an estimated time constant of 4.7 s and 10.9 s for **CZ-BO8**, **CZ-BO12** until the initial state is reached. Similar to the rising process for **CZ-BT8** and **CZ-BT12**, the two polymers have no quick decay but a sluggish photocurrent decrease with an estimated time constant of 23.9 s and 19.7 s, which is much slower than the BO series.

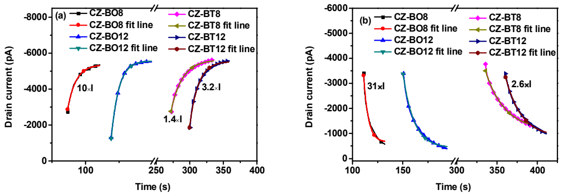


Fig. 7 Time response of photocurrent growth (a) and decay (b) for **CZ-BO8**, **CZ-BO12**, **CZ-BT8** and **CZ-BT12**. The circles are experimental points and the solid red lines fit to the exponential equations.

As a result, the photoresponse of the **CZ-BT8** and **CZ-BT12** seem to exhibit longer response time than the BO series. The quick growth rate may be due to the better crystallinity of BO based polymers. Additionally, the morphology of polymers based on BO was rougher than that based on BT, revealing that **CZ-BO8** and **CZ-BO12** as films formed larger aggregates(vide infra)..For the above reasons, BO based polymers exhibited higher hole mobility and faster phototransistor response.The long-range ordered molecular arrangement in the bulk crystals, small grain boundaries and few defects are good for the conduction of free charge carriers. The amorphous structure and imperfection of **CZ-BT8** and **CZ-BT12** films could capture the photon-generated excitons and lower the effective carrier density substantially, which decelerate the speed of the growth current. The longer decay time can also be explained by the same reasons mentioned above. When light illumination was turned off, the trapped excitons, as mentioned before, maybe be liberated and contributed to the current. Otherwise, we speculate that the longer exciton lifetime of the BT series may be a course for the low decay speed. When the light was off, the long lived excitons cannot disappear immediately, further dissociate to form free charge carriers, and collected by the electrodes, which also extend the current decrease time.

Film morphologies

AFM images of four polymers as thin films are shown in Figure 6. BT based polymer films exhibited a smoothsurfaceafter thermal annealing, demonstratingthe formed aggregates are mostly in small size.WhereasforBO based polymer films,large domains could be observed, which are probably ascribed to their better crystallinity.It is reasonable that BO based polymer films with higher crystallinity exhibit higher hole mobilityand better phototransistor properties.

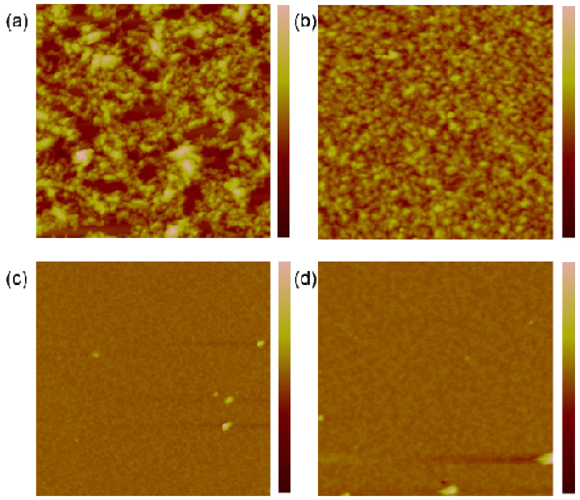


Fig.8AFM height images of polymer thin films (a) **CZ-BO8;** (b) **CZ-BO12;** (c) **CZ-BT8; and** (d) **CZ-BT12** (5 × 5 μm).

Conclusions

In summary, we have designed and synthesized four D–A alternating conjugated polymers and prepared organic thin film transistors and phototransistors with high performance.These four polymers are all soluble in common organic solvents at elevated temperature and suitable for the fabrication of photoconducting devices by solution processing. Hole mobilities of these polymers are in the range of 0.02 to 0.1 cm^2 V^{-1} s^{-1}, which make charge carrier transport and collection efficient and fast.The high mobility and the wide absorption in the visibleregion made main contributions to the high device performance, namely, a maximum on/off ratio of 8.2 × 10^3 and a maximum responsivityof 665 mA/W were obtained for benzooxadiazole containing polymer based phototransistors. Additionally, the fast response time of BO basedpolymers make them be suitable for the fabrication of high-speed photoswitches.

Acknowledgements

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Notes and references

1 Y. L. Guo, C. Y. Du, G.Yu, C. A.Di, S. D. Jiang, H. X. Xi, J.Zheng, S. K.Yan, C. L.Yu, W. P. Hu, Y. Q. Liu, *Adv. Funct. Mater.*, 2010, **20**, 1019.
2 Q. Tang, L.Li, Y. Song, Y. Liu, H.Li, W. Xu, W. Hu, D. Zhu, *Adv. Mater.*, 2007, **19**, 2624.
3 M. E,Gemayel, M. Treier, C. Musumeci, C. Li, K. Mullen, P. J.Samori,*J Am. Chem. Soc.*, 2012, **134**, 2429.
4 T. P. I. Saragi, R. Pudzich, T. Fuhrmann, J. Salbeck, *Appl. Phys. Lett.*, 2004, **84**, 2334.
5 K. S. Narayan, N. Kumar, *Appl. Phys. Lett.*, 2001, **79**, 1891.
6 W. Shockley, M. Sparks, G. K.Teal, *Phys. Rev.*, 1951, **83**, 151.
7 H. Dong, Z. Bo, W. Hu, *Macromol. Rapid Commun.*, 2011, **32**, 649.
8 F. Yan, J. H. Li, S. M. J. Mok, *Appl. Phys.*, 2009, **106**, 074501.
9 Y. Xu, P. R. Berger, J. N. Wilson, U. H. F. Bunz, *Appl. Phys. Lett.*, 2004, **85**, 4219.
10 S. M. Mok, F. Yan, H. L. W. Chan, *Appl. Phys. Lett.*, 2008, **93**, 023310.
11 Y. R. Liu, J. B. Peng, P. Lai, *Thin Solid Films,* 2008, **516**, 4295.
12 M. C. Hamilton, S. Martin, J. Kanicki, IEEE Trans. Electron Devices., 2004, **51**, 877.
13 M. C. Hamilton, J. Kanicki, *IEEE J. Sel. Top. Quantum Electron.*, 2004, **10**, 840
14 Q. Tang, L. Li, Y. Song, Y. Liu, H. Li, W. Xu, W. Hu, D. Zhu, *Adv. Mater.*, 2007, **19**, 2624.
15 H. S. Kang, C. S. Choi, W. Y. Choi, D. H. Kim, K. S. Seo, *Appl. Phys. Lett.*, 2004, **84**, 3780.
16 Y. Y. Noh, D. Y. Kim, Y. Yoshida, K. Yase, B. J. Jung, E. Lim, H. K. Shim, *Appl. Phys. Lett.*, 2005, **86**, 043501.
17 Y. Y. Noh, D. Y. Kim, K. J. Yase, *Appl. Phys.*, 2005, **98**, 074505.
18 T. P. I. Saragi, J. Londenberg, J. J. Salbeck, *Appl. Phys.*, 2007, **102**, 046104.
19 M. Mas. Torrent, P. Hadley, N. Crivillers, J. Veciana, C. Rovira, *Chem. Phys. Chem.*, 2006, **7**, 86.
20 Y. Yamamoto, T. Fukushima, Y. Suna, N. Ishii, A. Saeki, S. Seki, S. Tagawa, M. Taniguchi, T. Kawai, T. Aida, *Science*, 2006, **314**, 1761.
21 H. Dong, H. Li, E. Wang, H. Nakashima, K. Torimitsu, W. Hu, *J. Phys. Chem. C,* 2008, **112**, 19690.
22 N. S. Sariciftci, L. Simliowitz, F. Wudl, A. J. Heeger, *Science*, 1992, **258**, 1474.
23 G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science*, 1995, **270**, 1789.
24 X. Gong, D. Moses, A. J. Heeger, S. Liu, A. K.Y. Jen, *Appl. Phys. Lett.*, 2003, **83**, 183.

25 Y. Shao, X. Gong, A. J. Heeger, M. Liu, A. K.Y. Jen, *Adv. Mater.*, 2009, **21**, 1972.

26 E. Reichmanis, H. Katz, C. Kloc, A. Maliakal, *Bell Labs Technical Journal*, 2005, **10**, 87.

27 A. Facchetti, M. H. Yoon, T. Marks, *Adv. Mater.*, 2005, **17**, 1705.

28 Y. Sun, Y. Liu, D. Zhu, *J. Mater. Chem.*, 2005, **15**, 53.

29 H. Sirringhaus, *Adv. Mater.*, 2005, **17**, 2411.

30 S. Gunes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.,* 2007, **107**, 1324.

31 P. M. Beaujuge, W. Pisula, H. N. Tsao, S. Ellinger, K. Müllen, J. R. J. Reynolds, *J. Am. Chem. Soc.*, 2009, **131**, 7514.

32 Q. T. Zhang, J. M. J. Tour,*J. Am. Chem. Soc.*, 1998, **120**, 5355.

33 A. Ajayaghosh, *Chem. Soc. Rev.*, 2003, **32**, 181.

34 R. Qin, W. Li, C. Li, C. Du, H. F. Schleiermacher, M. Andersson, Z. Bo, Z. Liu, O. Inganas, U.Wuerfel, F. Zhang, *J. Am. Chem. Soc.*, 2009, **131**, 14612.

35 X. Gong, M. Tong, Y. Xia, W. Cai, J. Moon, Y. Cao, G. Yu, C. Shieh, B. Nilsson, A. J. Heeger, *Science,* 2009, **325**, 1665.

36 S. T. Lee, “Metal Interfaces in Organic Electronic Devices - New Insights to Traditional Concepts”, in: Organic Electronics: Materials, Processing, Devices and Applications, F. So, Ed., CRC Press, Boca Raton, FL 2009.

37 M. C. Hamilton, S. Martin, J. Kanicki, *IEEE Trans. Electron DeV.,* 2004, **51**, 877.

38 S. Martin, M. C. Hamilton, J. Kanicki, *Proc. IDRC*, 2003, **14**.

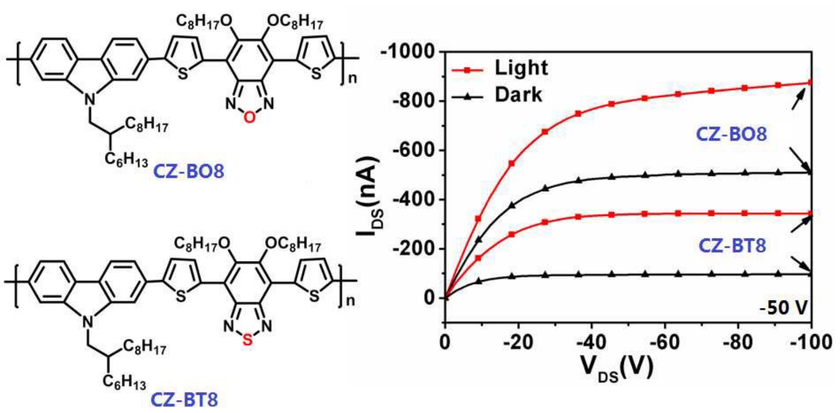
39 M. C. Hamilton, J. Kanicki, *IEEE J. Sel. Top. Quantum Electron.,* 2004, **10**, 840.

40 W. Hu, H. Nakashima, K. Furukawa, Y. Kashimura, K. Ajito, Y. Liu, D. Zhu, K. Torimitsu, *J. Am. Chem. Soc.*, 2005, **127**, 2804.

41 B. Chitara, L. S. Panchakarla, S. B. Krupanidhi, C. N. R. Rao, *Adv. Mater.*, 2011, **23**, 5419.

42 D. B. Farmer, R. Golizadeh-Mojarad, V. Perebeinos, Y. M. Lin,G. S. Tulevski, J. C. Tsang, P. Avouris, *Nano Lett.*, 2009, **9**, 388.

Graphic abstract



Benzooxadiazole and benzothiadiazole based conjugated polymers have been synthesized and used for the fabrication of high performance phototransistors