Nonvolatile Rewritable Memory Effects in Graphene Oxide Functionalized by Conjugated Polymer Containing Fluorene and Carbazole Units

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Dedicated to Professor Dr. Dr. h.c. Michael Hanack on the occasion of his 80th birthday

Abstract: A new polymer, poly[{9,9di(triphenylamine)fluorene}(9,9-dihexylfluorene)(4-aminophenylcarbazole)] (PFCz) was synthesized and used in a reaction with graphene oxide (GO) containing surface-bonded acyl chloride moieties to give a soluble GObased polymer material GO–PFCz. A bistable electrical switching effect was observed in an electronic device in which the GO–PFCz film was sandwiched between indium–tin oxide (ITO) and Al electrodes. This device exhibited two accessible conductivity states, that is, a low-conductivity (OFF) state and a high-conductivity (ON) state, and can be switched to the ON state under a negative electrical sweep; it can also be reset to the initial OFF state by a reverse (positive) electrical sweep. The ON state is nonvolatile and

Keywords: graphene oxide • molecular devices • polyfluorene • polymers • rewritable memory can withstand a constant voltage stress of -1 V for 3 h and 10^8 read cycles at -1 V under ambient conditions. The nonvolatile nature of the ON state and the ability to write, read, and erase the electrical states, fulfill the functionality of a rewritable memory. The mechanism associated with the memory effects was elucidated from molecular simulation results and in-situ photoluminescence spectra of the GO–PFCz film under different electrical biases.

Introduction

Graphene, which was discovered most recently, has attracted considerable interest owing to the long-range π -conjugation yielding extraordinary thermal, mechanical, and electrical properties.^[1–9] Its two-dimensional (2D) network is the fundamental building block of other carbon-based materials, such as 0D fullerene, 1D carbon nanotubes, 3D graphite and 3D diamond. The chemistry of graphene reported in the literatures mainly concerns the chemistry of graphene oxide (GO) with chemically reactive oxygen functionalities, including carboxylic acid groups at the edges of GO, and

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epoxy and hydroxyl groups on the basal planes.^[3,10] Both small molecules and polymers have been covalently attached to the GO's highly reactive oxygen functionalities, or non-covalently attached on the graphitic surfaces of chemically modified graphenes, for potential use in polymer composites, paperlike materials, sensors, photovoltaic applications, and drug-delivery systems.^[3]

Our current interet in the chemical modification and functionalization of GO mainly involves the GO-based polymer memories. In comparison to inorganic-materials-based memory devices, molecular and polymeric memories exhibit low-cost potential, simplicity in structure, good scalability, potential for high-density data storage in 3D arrays, and possibility of fabricating flexible devices.^[11] Reversible switching characteristics of organic nonvolatile memory transistors (ONVMTs) using GO nanosheets as a chargetrapping layer have been reported by Jen et al.^[12] The transfer curves of GO-based ONVMTs showed large gate-biasdependent hysteresis with threshold voltage shifts over 20 V. In our previous work, we designed and synthesize a novel conjugated triphenylamine-based polyazomethine (TPAPAM), covalenty grafted onto graphene oxide (GO-TPAPAM), and placed the resulting films within aluminum and indium-tin oxide contacts.^[13] The GO-TPAPAM-based memory device exhibited the bistable electrical switching and nonvolatile rewritable memory effect. A soluble GO functionalized with poly(N-vinylcarbazole) (GO-PVK) was also prepared by covalent coupling of GO-TDI (TDI=toluene-2,4-diisocyanate) with end-functionalized PVK (PVK-

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DDAT: DDAT = S-1-dodecyl-S'-(α, α' -dimethyl- α'' -aceticacid)trithiocarbonate).^[14] This material could also be used as a two-state electronic memory element. We used model calculations to explain these observations, and found that the polymer coats the GO sheets and acts as a tunneling barrier for electrons moving from one GO sheet to another. The "ON-OFF" transition process is perfectly reversible, as the application of a high enough positive voltage can induce the reverse transfer of electrons, reducing the conductivity back to its initial value. Very recently we prepared a GO-polymer complex, consisting of GO nanosheets with covalently grafted poly(tert-butyl acrylate) (PtBA) brushes, by means of surface-initiated atom-transfer radical polymerization (ATRP).^[15] The grafted hydrophobic polymer brushes substantially enhance the solubility of GO in organic solvents, and the GO-g-PtBA nanosheets can form a uniform and stable dispersion in toluene. The functionalized GO nanosheets can also be integrated into an electroactive polymer matrix. Bistable electrical-conductivity switching behavior and a nonvolatile electronic memory effect were demonstrated in a composite thin film of poly(3-hexylthiophene) (P3HT) containing 5 wt% GO-g-PtBA in an Al/GO-g-PtBA+P3HT/ITO sandwich structure. The molecular-structure-dependent memory effects demonstrate that it is possible to tune the electrical switching behavior in a GO-polymer complex by tailoring molecular structures of the attached polymer segments.

In this contribution, we first synthesized a new conjugated polymer, poly[{9,9-di(triphenylamine)fluorene}(9,9-dihexyl-fluorene)(4-aminophenylcarbazole)] (PFCz), and then this polymer was used in a reaction with GO containing surface-bonded acyl chloride moieties to give a soluble GO-based polymer material GO–PFCz (Scheme 1). This polymer also shows a nonvolatile rewritable memory effect, with a turn-on voltage of about -1.3 V and an ON/OFF state current ratio of more than 10^3 .

Results and Discussion

The covalent attachment of PFCz onto GO through the amide linkage was confirmed by the IR spectra (Figure 1) and XPS spectra (Figure 2). The main characteristic absorption bands in the IR spectrum of GO are located at 1733 (C=O carbonyl stretching of -COOH), 1412 (O-H deformation vibration), 1226 (C-OH stretching) and 1053 cm⁻¹ (C-O stretching). Upon treatment with PFCz, the bands at 1732 and 1412 cm⁻¹ disappeared, followed by the appearance of a new vibration band at about 1667 cm⁻¹, which is assigned to the stretching mode of the amide linkage. The vibration at 1590 cm⁻¹ is attributed to C–NH₂ stretching, implying that residual unreacted NH2 groups still remain in the resulting GO-PFCz material. The N1s XPS spectrum of PFCz clearly indicated that the peaks of nitrogen functionalities appeared at 399.93 (the N in Ph_3N) and 401.17 eV (the N in NH_2). In contrast to PFCz, an additional component at 398.46 eV cor-



Scheme 1. Synthesis of GO-PFCz.



Figure 1. FTIR spectra of a) GO, b) PFCz, and c) GO-PFCz.

responding to N bound to the carbonyl C (i.e., NH–C=O) was observed in the N1s XPS spectrum of GO–PFCz.

As shown in Figure 3, the main absorption peak of PFCz is located at 302 nm. After covalent attachment onto the surface of GO, the largest absorption peak is shifted to the blue by $\Delta \lambda = 5$ nm as a result of the possible electron transfer from PFCz, as electron donor, to GO, as electron acceptor. The absorption shoulder of GO–PFCz is significantly re-

Chem. Eur. J. 2011, 17, 10304-10311

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Figure 2. The N1s XPS spectra of a) PFCz and b) GO-PFCz.



Figure 3. UV/Vis absorption spectra of the samples in THF.

duced, probably owing to the fact that incorporation of the carbazole group reduces the effective conjugation of the fluorene backbone.^[16] The weak and featureless absorption in the 420–600 nm region of the GO–PFCz indicates presence of the GO group.^[17]

The fluorescence measurements of PFCz and GO–PFCz were carried out in THF by applying 370 nm as excitation wavelength (Figure 4). The intensity of the emission band of GO–PFCz at 415 nm was a little bit quenched when compared to that of PFCz suggesting energy and/or electron transfer between the excited singlet states of the PFCz moiety and the GO moiety. In addition, the absolute fluorescence quantum yields (ϕ_{PL}) of PFCz and GO–PFCz are 0.31 and 0.24, respectively. To further study this fluorescence quenching effect, we measured the absolute fluorescence





Figure 4. Steady-state fluorescence spectra of the samples in THF; λ_{ex} = 370 nm.



Figure 5. Cyclic voltammogram of the GO–PFCz film on Pt with Bu_4NCIO_4 as the supporting electrolyte at ambient temperature. Scan rate: 15 mV s^{-1} .

quantum yields of the mixture of GO and PFCz in THF, with different GO concentrations. With the increase in GO concentration from 1 to 2 to 5 to 10 wt %, the fluorescence quantum yield of the mixture exhibits a significant decrease (from 0.30 to 0.28 to 0.23 to 0.17).

The electrochemical properties of the GO–PFCz film coated on a Pt disk electrode, as shown in Figure 5, were measured by cyclic voltammetry (CV) in deaerated acetonitrile containing recrustallized Bu₄NClO₄ (0.10 M) at room temperature. All potentials (*vs* Ag/Ag⁺) were converted to values versus SCE by adding 0.29 V.^[18] Its first oxidation and reduction potentials were found to be +1.23 and -0.85 V versus Ag/Ag⁺, respectively, which correspond to +1.52 and -0.56 V versus SCE, respectively. The HOMO/LUMO values of GO–PFCz were experimentally calculated by the onset of the redox potentials taking the known reference level for ferrocene, 4.8 eV below the vacuum level, according to the Equation (1):^[19]

$$HOMO/LUMO = -(E_{onset} - E_{ox(ferrocene)}) - 4.8 \text{ eV}$$
(1)

In our electrochemical experiments ferrocene exhibited an oxidation peak with an onset of 0.38 V versus Ag/AgCl. The calculated HOMO and LUMO values were -5.65 and -3.57 eV, respectively. The calculated HOMO-LUMO bandgap (E_g^{CV}) is found to be 2.08 eV. The values of the ionization potential (IP) and the electron affinity (EA) can also be estimated from these onset potentials (vs. SCE) by using Equations (2) and (3),^[20] in which the constant 4.39 is the relationship between IP, EA, and the electrochemcial potentials.^[21] The calculated IP and EA values are 5.91 and 3.83 eV, respectively.

$$IP = E_{\text{first oxidation}} + 4.39 \,\text{eV} \tag{2}$$

$$\mathbf{EA} = E_{\text{first reduction}} + 4.39 \,\mathrm{eV} \tag{3}$$

The electrical switching and memory effects of GO-PFCz are demonstrated by the J-V characteristics of an electronic device with the GO-PFCz film sandwiched between the ITO and Al electrodes, as shown in Figure 6a. The device was initially in the low-conductivity (OFF) state. During the first negative sweep (with Al as the cathode and ITO as the anode) from 0 to -4 V, the device exhibited an abrupt increase in current density at -1.3 V, indicating the electrical transition from the initial OFF state to the high-conductivity (ON) state. This switch-on process is equivalent to the "writing" process in a digital memory cell. The ON/OFF current ratio is more than 10^3 at -1 V. The ON state is stable and can be retained even after turning off the power supply (the second sweep), indicating the nonvolatile nature of the ON state. When a positive sweep from 0 to 4 V was applied (the thrid sweep), the ON state was reset to the initial OFF state at +3.3 V. This switch-off process is equivalent to the "erasing" process of a digital memory cell. The device is thus erasable and allows for application in a rewritable data storage system. The subsequent fourth sweep was applied after removing the power supply. The device was found to retain the low-conductivity state, indicating its good stability in the OFF state. The ability to write, read, and erase the electrical states, as well as the nonvolatile nature of the ON and OFF states, fulfill the functionality of a flash-type memory. As indicated by the subsequent fifth to twelfth sweeps, the above write-read-erase-read switching cycles can be repeated with good accuracy, except for slight variations in the switching threshold voltages, associated probably with inherent relaxation property of the polymer chain.^[22] Figure 6b shows the effect of operation time on the stability of the GO-PFCz device. Under a constant stress of -1 V, no evident degradation in current density was observed for both the ON and OFF states over a 3 h period. In addition, the two electrical states were also able to withstand 10^8 read pulses of -1 V, as shown in Figure 6c.

To gain insights into the above electrical switching effects, computational studies have been performed on the GO–PFCz using density functional theory (DFT) method at the B3LYP/6-31G(d) level. The accuracy of these methods for the calculation of electron affinities of aromatic compounds has been demonstrated by Schaefer et al.^[23] To save computing resources, a simplified GO–PFCz model was employed for the calculation. In the model, the GO moiety contains 16 aromatic rings together with four kinds of oxygen func-



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Figure 6. a) Current-density-voltage (J-V) characteristics of a 0.4×0.4 mm² ITO/GO-PFCz/Al device. The sequence and direction of each sweep are indicated by the respective number and arrow. b) Effect of operation time on the ON and OFF state currents of the ITO/GO-PFCz/Al device under a constant stress of -1 V. c) Effect of read pulses of -1 V on the ON and OFF state currents of the ITO/GO-PFCz/Al device. The insets of c) show the pulse used for measurement.

tionalities, that is, epoxide, hydroxyl, carbonyl and carboxyl, and the polymer segment contains one repeat unit, including all the functional moieties. The first three highest occupied molecular orbitals (HOMO, HOMO2, and HOMO3) and the lowest unoccupied molecular orbitals (LUMO) of the GO–polymer model, as well as the plausible electronic transitions under excitation, are depicted in Figure 7. The LUMO of GO–PFCz is located on the GO moiety, indicat-

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Figure 7. Calculated molecular orbitals of the basic unit and the plausible electronic transitions under the excitation of GO-PFCz.

ing that the GO moiety may act as the electron acceptor. The first three highest occupied molecular orbitals (HOMO, HOMO2, and HOMO3) are located on the triphenylamine, GO and fluorene moieties, respectively, indicating that all the functional moieties are able to donate electrons.

In the as-cast GO-PFCz film, the oxygen functionalities introduce a number of defect sites composed of sp³-hybridized carbon atoms; these defects limit the in-plane charge transportation in the GO nanosheet.^[24] In addition, the attached polymer segment tends to intercalate between the neighboring GO nanosheets and acts as a tunneling barrier for the transverse charge transportation.^[25] As a result, the as-fabricated GO-PFCz device remained in the low conductivity (OFF) state during the initial electrical sweep. At the switching threshold voltage, electrons transit readily from HOMO2 to the LUMO within the GO moiety, forming a locally excited state. Electron transition from the HOMO and HOMO3 to the LUMO, however, is inhibited, due to the absence of overlapping between LUMO and the two HOMOs. Alternatively, electrons in HOMO3 can overcome the energy barrier between HOMO3 and HOMO2 (0.33 eV) and fill the generated holes in HOMO2, followed by spontaneous electron transition from HOMO to HOMO3. As a result, the excited electrons in LUMO can reside in the GO nanosheet and delocalize among the giant π -conjugation system. Due to the strong reducibility, these electrons can probably reduce the GO to graphene. In the partially reduced GO nanosheet, the defect sites associated with oxygen functionalities are significantly eliminated, allowing a better electron delocalization and transportation in both in-plane and transverse directions. The device is thus switched from the OFF state to the ON state. The above electric-field-induced charge-transfer (CT) in GO-PFCz is consistent with the previously reported photoinduced CT between graphene and functionalized polyfluorene^[26] or CdSe nanoparticles.^[17,27] Due to the giant π -conjugation plane, the electrons can delocalize throughout the GO nanosheet, making the conductive CT state stable even after removing the applied bias. The flexible amide linker between GO and polymer segment can also inhibit dissociation of the CT complex. A nonvolatile ON state is thus observed. However, a reverse positive bias with sufficient energy can extract electrons from the graphene nanosheet, returning the device back to the initial OFF state. In addition, as elucidated by the UV/Vis absorption and fluorescence spectra, incorporation of the carbazole group interrupts the effective conjugation and intrachain ordering of the fluorene backbone.[16b,28] Therefore, charge migration along the polymer backbone is limited in the pre-excited GO-PFCz molecule, resulting in a lower OFF state current $(3.4 \times 10^{-2} \text{ A cm}^{-2} \text{ for})$ GO–PFCz at -1 V).

To elucidate the above electric-field-induced CT process, in situ fluorescence spectra of the GO–PFCz film in an ITO/ polymer/Al sandwich device under electrical biases were studied (Figure 8). The electrical bias was applied on the Al electrode, with ITO as the ground electrode. All the emission spectra obtained at the excitation wavelength of 320 nm display a maximum fluorescence peak at 396 nm and a shoulder peak at around 430 nm, arising probably from the conjugated backbone of the polymer segments.^[29] When a negative bias (-4 V) larger than the switch-on threshold voltage (-1.3 V) is applied on the GO–PFCz device, electri-

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Figure 8. In situ PL spectra of the GO–PFCz film in an ITO/polymer/Al sandwich device under electrical biases. OFF-1 denotes the emission spectrum before applying any electric bias, while ON-1 to OFF-3 denote, respectively, the emission spectra after applying the respective electrical bias indicated in the bracket (with Al as the working electrode and ITO as the ground electrode).

cal switching from the OFF state to the ON state is triggered, as shown in Figure 6a. The resultant fluorescence spectrum (ON-1 spectrum) shows a decrease in the emission intensity in comparison to the initial fluorescence spectrum (OFF-1 spectrum). This partial fluorescence quenching arises probably from CT from the polymer segment to the GO moiety. As a result, the conductive CT state is formed, and the device is switched to the ON state. When a positive electrical sweep is applied on the GO-PFCz device, for example, the 3th sweep in Figure 6a, electrons in the graphene nanosheet are extracted and the CT state is dissociated. The device is thus switched back to the initial OFF state. The erasing of the ON state is supported by recovery of the initial fluorescence spectrum corresponding to the OFF state after applying a positive bias of +4 V (OFF-2 spectrum). The slight decrease in the OFF-2 spectrum in comparison to the OFF-1 spectrum is probably associated with a delay in conformational change of the polymer chain in response to change in the electrical field.^[30] The "ON-OFF" changes in the fluorescence spectra match the write-erase processes in the J-V characteristics of the GO-PFCz device, and can be repeated with good accuracy, as indicated by the subsequent ON-2, OFF-3, and ON-3 spectra.

As we discussed above, the working mechanism in our memory device is due to charge transfer. The charge-transfer processes and the switching characteristics are independent of the choice of electrodes.^[31] Although the turn-on voltage of the device may vary only slightly with the electrode work functions, the memory characteristics (worm/flash/dram), the on/off ratio and the device stability are unrelated to the used electrodes.

Conclusion

A new solution-processable GO-PFCz polymer was synthesized and characterized for its electrical switching and

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memory effects. A device based on this material can be switched "ON" and "OFF" during the negative and positive electrical sweeps, respectively. Electric-field-induced chargetransfer (CT) from the polymer donor to the GO acceptor gives rise to a conductive CT state, resulting in the electrical transition from the initial OFF state to the ON state. However, a reverse bias can dissociate the CT state and reset the device back to the initial OFF state. The electric-field-induced CT process is supported by fluorescence quenching and recovery in the in situ fluorescence spectra of the GO– PFCz film under electrical biases. Incorporation of carbazole group in the GO–PFCz molecule can result in a larger switch-off threshold voltage and a higher ON/OFF current ratio.

Experimental Section

General: All chemicals were purchased from Aldrich and used without further purification. Organic solvents were purified, dried, and distilled under dry nitrogen. Purified natural graphite was purchased from Shanghai Yifan Graphite Co. GO was prepared from graphite by the Hummers method, and dried for 10 days over P2O5 in a vacuum oven before use.[14b] 2,7-Dibromo-9,9- di(triphenylamine)fluorene (4) was prepared according to the literature.^[32]The UV/Vis absorption spectral measurements were carried out with a Shimadzu UV-2450 spectrophotometer. FTIR spectra were recorded on a Nicolet Nagma-IR 550 spectrophotometer using KBr pellets. Steady-state fluorescence spectra were measured on a HORIBA Jobin Yvon FluoroMax-4 spectrofluorometer, and the absolute fluorescence quantum yields were measured by integrating sphere method on the same instrument. The samples for fluorescence measurement were dissolved in dry THF, filtered, and transferred to a long quartz cell, and then capped and bubbled with high purity argon for at least 15 min before measurement. NMR spectra were recorded on a Bruker 400 spectrometer at a resonance frequency of 400 MHz for ¹H NMR spectra in deuterated solution with a tetramethylsilane (TMS) as a reference for the chemical shifts. XPS measurements were carried on a Kratos AXIS HSi spectrometer with a monochromatized Al KR X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and pass energy of 40 eV. Molecular weights [number-average (M_n) and weight-average (M_w)] were determined with a Waters 2690 gel-permeation chromatograph (GPC) using a polystyrene standards eluting with tetrahydrofuran. Cyclic voltammetry was performed on an ALS630B electrochemical analyzer in deaerated benzonitrile containing recrystallized tetrabutylammonium perchlorate (Bu₄NClO₄, 0.1 M) as the supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm²) and a platinum wire as the counter electrode. The Pt working electrode (Bioanalytical System(BAS), Inc.) was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/AgNO₃ (0.01 M) reference electrode. All electrochemical measurements were carried out under an atmospheric pressure of argon. Device fabrication: The indium-tin oxide (ITO) glass substrate was carefully precleaned sequentially with deionized water, acetone, and 2-propanol in an untrasonic bath for 15 min, and then treated with oxygen plasma. A solution (100 µL) the functionalized graphene derivative (10 mgmL⁻¹) in N,N-dimethylacetamide (DMAc) was spin-coated onto the ITO substrate at a spinning rate of 1000 rpm, followed by solvent removal in a vacuum oven at 10⁻⁵ Torr and 50 °C for 10 h. The thickness of the polymer layer was about 50 nm, as determined by the AFM edge profiling. Finally, an Al top electrode of about 400 nm in thickness was thermally deposited onto the material surface through a shadow mask at a pressure of about 10⁻⁷ Torr. Electrical property measurements were carried out on devices of 0.4×0.4 mm², 0.2×0.2 mm², and 0.15×0.15 mm² in size, under ambient conditions, using an Agilent 4155C semiconductor

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parameter analyzer equipped with an Agilent 41501B pulse generator. The current-density-voltage (J-V) data reported here were based on the device unit of 0.4×0.4 mm² in size, unless stated otherwise. ITO was maintained as the ground electrode during the electrical measurements.

Molecular simulation: Molecular simulation of GO–PFCz was carried out with the Gaussian $03^{[33]}$ program package on a Hewlett–Packard Xeon Two Sockets Quad-Core workstation with 8 CPUs and 16 GByte memory. Molecular orbitals and their energy levels were calculated with density function theory (DFT) in B3LYP/6–31G(d) level. Vibrational frequencies were calculated analytically to ensure that the optimized geometries really correspond to the total energy minima.

Synthesis of 9-(4-nitrophenyl)-9*H*-carbazole (1): A stirred solution of 1bromo-4-nitrobenzene (14.47 g, 72 mmol), carbazole (10.02 g, 60 mmol), K₂CO₃ (8.29 g, 60 mmol), 1,10-phenanthridine (2.16 g,12 mmol) and CuI (2.27 g,12 mmol) in DMF (100 mL) was heated at 155 °C for 24 h. After cooling down to room temperature, ice-water (500 mL) was poured into the reaction mixture. The collected yellow soild was washed with distilled water and methanol for several times, respectively, and dried at 50 °C for 6 h under reduced pressure. Yield: 15 g (88 %). ¹H NMR (CDCl₃, 500 MHz): δ =8.46 (m, 2H), 8.14 (d, *J*=8 Hz), 2H, 7.78 (m, 2H), 7.49 (d, *J*=8 Hz, 2H), 7.44 (m, 2H), 7.34 ppm (m, 2H); EI-MS: *m/z*: 288.1 [*M*⁺].

Synthesis of 3,6-dibromo-9-(4-nitrophenyl)-9*H*-carbazole (2): Comopund 1 (8.67 g, 30 mmol) and *N*-bromosuccinimide (NBS, 11.74 g, 66 mmol) were stirred in anhydrous DMF (50 mL) at 0 °C for 48 h; then ice-water (500 mL) was added to the system, The collected yellow precipitate was washed with water and methanol for several times, respectively, and dried at 50 °C for 6 h under reduced pressure. Yield: 10 g (75%). ¹H NMR (CDCl₃, 500 MHz): δ =8.51–8.49 (m, 2H), 8.21 (d, *J*=8 Hz, 2H), 7.76–7.73 (m, 2H), 7.57–7.54 (m, 2H), 7.34–7.32 ppm (d, *J*=8 Hz, 2H); EI-MS: *m/z*: 445.9 [*M*⁺].

of poly[{9,9-di(triphenylamine)fluorene}(9,9-dihexylfluor-Synthesis ene)(4-nitrophenylcarbazole)] (PFNCz): A mixture of 2 (76 mg, 0.17 mmol), 3 (200 mg, 0.341 mmol), 4 (137 mg, 0.17 mmol), [Pd(PPh₃)₄] (2 mg, 0.002 mmol), K_2CO_3 (276 mg, 2 mmol), toluene (4 mL), and distilled water (1 mL) in a Schlenk tube was stirred at 80°C for 36 h. Then an excess phenylboronic acid (200 mg) and bromobenzene (200 mg) were added as end-capping reagents sequentially in 12 h interval. The mixture was extracted with chloroform (10 mL) three times, and the combined organic extracts were washed with water, brine, and dried over sodium sulfate. The salt was filtered off, and the filtrate was concentrated into a small volume. The polymer solution was added dropwise into stirred methanol. After filtration, the collected solid was purified by reprecipitating into methanol and then Soxhlet extraction with acetone. The polymer was then dried under vacuum to give a pale yellow solid (213 mg, yield 78%). ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.0-8.3$ (m, 4H), 7.3-7.9 (m, 20H), 6.7-7.2 (m, 34H), 1.91-2.10 (m, 8H), 0.92-1.10 (m, 24H), 0.51–0.77 ppm (m, 20H).

Synthesis of poly[{9,9-di(triphenylamine)fluorene}(9,9-dihexylfluorene)(4-aminophenylcarbazole)] (PFCz): A mixture of PFNCz (200 mg) and SnCl₂:2 H₂O (250 mg) in THF (40 mL) was refluxed for 6 h. The mixture was concentrated under reduced pressure and treated with H₂O (40 mL) and the pH was adjusted to 9 by treatment with 10% aqueous NaOH. The mixture was extracted with CHCl₃ (60 mL) the organic layers were washed with saturated brine and H₂O and dried. After removal of the solvent and dried under vacuum, a yellow solid (178 mg) was obtained. ¹H NMR (CDCl₃, 500 MHz): δ = 8.0–8.3(m, 2H), 7.3–7.9-(m, 22H), 6.7–7.2 (m, 34H), 3.79–3.85 (s, 2H), 1.91–2.10 (m, 8H), 0.92–1.10 (m, 24H), 0.51–0.77 ppm (m, 20H); GPC (THF, linear polystyrene as reference): M_n = 1.16×10⁴, M_w/M_n = 1.78.

Synthesis of GO–PFCz: GO with carboxylic acid groups (15 mg) was treated with a large excess of $SOCl_2$ containing a catalytic amount of DMF under reflux for 24 h. The residual thionyl chloride and solvent were removed by distillation. The obtained GO with surface-bonded acryl chloride moieties (GO–COCl) was directly used in the reaction with of PFCz (150 mg) containing side-chain NH₂ groups in DMF (50 mL) at 130 °C for 3 days under argon in the presence of triethylamine (Et₃N, 3 mL). After cooling to room temperature, a large amount of

water was added to the above reaction mixture to remove the triethylammonium salts formed during the reaction. The crude product was collected by filtration, re-dissolved in a small amount of DMF, and then precipitated from MeOH/H₂O (v/v=1:1) solution (this procedure was repeated at least 3 times). The resulting material (124 mg) was dried in vacuum at 65 °C for 2 days.

Acknowledgements

The authors are grateful for the financial support of the National Natural Science Foundation of China (21074034), the Ministry of Education of China (309013), the Fundamental Research Funds for the Central Universities, the Shanghai Municipal Educational Commission for the Shuguang fellowship (08GG10) and the Shanghai Eastern Scholarship.

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Received: March 16, 2011 Published online: July 29, 2011

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