

View Article Online View Journal

Journal of Materials Chemistry C

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: W. Xue, Y. Zhang, J. Duan, D. Liu, Y. Ma, N. Shi, S. Chen, L. Xie, Y. Qian and W. Huang, *J. Mater. Chem. C*, 2015, DOI: 10.1039/C5TC00819K.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/materialsC

RSC Publishing

Paper

Cite this: DOI: 10.1039/x0xx00000x

Journal of Materials Chemistry C

Received 00th January 2015, Accepted 00th January 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 01 July 2015. Downloaded by Freie Universitaet Berlin on 07/07/2015 03:47:19.

A Highly Sensitive Fluorescent Sensor Based on Small Molecule Doped in Electrospun Nanofibers: Detection of Explosives as well as Color Modulation

Wei Xue,^{*a*} Yang Zhang,^{*a*} Juanjuan Duan,^{*a*} Dong Liu,^{*a*} Yawei Ma,^{*a*} Naien Shi,^{**a*} Shufen Chen,^{*a*} Linghai Xie,^{**a*} Yan Qian^{*a*} and Wei Huang^{**a*,*b*}

Fluorescent polymer nanofibers have wide applications in the fields of nano-photonics, nanooptoelectronics, chemical sensors and light-emitting diodes. It is a distinguished substitute route to dope small fluorophore into a type of low-cost polymer in case of acquiring costeffective and high-performance optical materials. In order to get a deep insight into the photophysical process in the small molecule accommodating polymer nanofiber system, and obtain a highly sensitive and cost-effective explosive fluorescent sensor, a new type of highly sensitive low-cost sensor towards nitro-compounds based on PEO/MePyCz (polyethylene oxide/ 4-(2-(2-methoxyethoxy)ethoxy)-9-(pyren-1-yl)-9H-carbazole) composite nanofibers was synthesized. It exhibited fast response and high quenching efficiency towards DNT vapor, which may be attributed to an improved exciton migration for MePyCz in PEO, apart from the large driving force of the electron transfer and the nanofibrous structures. Besides, it promoted a fluorescence resonance energy transfer process in the polymer fibrous matrix with a green-emitting material of 2-(thiophen-2-yl)-fluoren-9-one. The sensing composite nanofibrous film had good sensitivity and selectivity and might be constructed into a portable detector for explosives.

Introduction

Fluorescent polymer nanofibers are of great interest because they can serve as important elements in many fields, such as nanophotonics, nano-optoelectronics, chemical and biological sensors, organic semiconductors and light-emitting diodes, due to their fascinating properties of flexibility, charge transport ability and hospitality.¹⁻⁸ Electrospinning is an efficient high throughput method to prepare light-emitting conjugated polymer nanofibers, which is based on stretching a polymer solution under electrostatic forces, although there are also other approaches of supramolecular assembly, covalent synthesis, physical drawing, nanolithography.9, 10 Generally, artificial synthetic conjugated fluorescent polymers are generally of high cost with cumber preparation procedures. It is a distinguished substitute route to dope small optoelectronic molecules into a type of low-cost polymer to act as the active components in optoelectronic devices and sensors.¹¹⁻¹⁵ In this case, it is of great importance to investigate the photophysical process (exciton migration, electron transfer, energy transfer, etc.) in the small molecule accommodating polymer nanofibers.

As we know, the explosive detection is very important for the applications in homeland safety, industrial process safety control, and daily life. Fluorescent sensing is an effective and extensively applied method to detect explosives, because of its short response time, excellent sensitivity, simplicity, and cost-effectiveness, in comparison with the currently widely used analytical laboratory methods of chromatography,¹⁶⁻¹⁹ ion mobility spectrometry,²⁰ Raman

spectroscopy,²¹ and X-ray diffraction.²² It is a great challenge to explore highly effective explosive vapor sensing materials since sensing in vapor of explosives is very important whereas the vapor pressure is extremely low, and great efforts have been paid on prominent fluorescent sensors. Conjugated polymers (pentriptycene, diarylpoly(acetylene), poly(phenyl-co-fluorene) or spirofluorene),^{23,} ²⁴ organic nanorods (alkoxycarbonyl-substituted, carbazole-cornered, arylene-ethynylenetetracycles),²⁵ quantum dots²⁶ (for example, amine-capped ZnS-Mn²⁺ nanocrystals etc.) and microporous metalorganic frameworks²⁷⁻²⁹ (benzene carboxlates, triphenylene carboxylates, and etc.) are proven to be high-performance fluorescent sensing materials. However, the wide applications of the reported materials are limited by costly, complicated and low-yield synthesis procedures, or harsh synthetic environment. There is still a great need not only to fabricate highly sensitive and cost-effective fluorescent sensors, but also to realize the large-scale fabrication.

Considering the intrinsic delocalized pi-electrons and blue emission of pyrene and good charge-transporting capability of carbazole as well as the convenience and low cost of the two units, a new kind of fluorescence sensing material of alkoxy substituted carbazole pyrene was designed, synthesized and doped into a widely applied low-cost polymer of polyethylene oxide (PEO), so as to obtain a type of high-performance and cost-effective explosive fluorescent sensor, which is also employed as a model system to study the photophysical process in hybrid fluorescent polymer nanofibers. The structure of the sensing material, 4-(2-(2-(2methoxyethoxy))ethoxy)-9-(pyren-1-yl)-9H-carbazole

(MePyCz), was shown in Scheme 1. At a doping content of 0.50

wt% for MePyCz into PEO, the hybrid fluorescent polymer nanofibers exhibit a high quenching efficiency of 73% at 2h exposure towards DNT, which is 2.6 fold as compared with that of reported porphyrin TMOPP/ polystyrene solid nanofibers of ca. 28%.³⁰ The exciton migration in the hybrid materials played a key role in the fast response to the analyte agents. Besides, the doped MePyCz are found to perform efficient fluorescence energy transfer with an energy acceptor of ThFO in the PEO polymer nanofibers.

Experimental

Materials

Published on 01 July 2015. Downloaded by Freie Universitaet Berlin on 07/07/2015 03:47:19.

2-(2-(2-methoxy)ethoxy)ethanol, 4-methylbenzene-1-sulfonyl chloride (TsCl), 9H-carbazol-4-ol, 9H-carbazole, 1-bromopyrene, cuprous iodide (CuI), 18-crown-6, potassium carbonate (KCO₃) 1,2dichlorobenzene, sodium hydroxide (NaOH), potassium fluoride (KF), sodium chloride (NaCl), naphathalene, urea and magnesium sulfate (MgSO₄) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. 2-bromo-9H-fluoren-9-one was offered by Puyang HuiCheng Chemical Co., Ltd. Thiophen-2-ylboronic acid (ThB(OH)₂) and Pd(PPh₃)₄ were supplied by Sahn Chemical Technology Co., Ltd. Polyethylene oxide (PEO) with Mw=200000 was purchased in the United States. 2,4-dinitrotoluene (DNT) was obtained from Sigma-Aldrich Chemical Reagent. p-nitrotoluene (p-NT) was purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. Nitrobenzene (NB), nitromethane (NM) and benzophenone (BP) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Picric acid (PA) was purchased from Guangdong Xilong Chemical Co., Ltd. Tetrahydrofuran (THF), ethanol (EtOH), petroleum ether (PE), 1,2-dichloromethane (CH₂Cl₂), toluene, 1, 2dichlorobenzene and chloroform (CHCl₃) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. All reagents and solvents were used as received without further purification.



Scheme 1. The synthesis procedure of 4-(2-(2-(2-methoxy)ethoxy)ethoxy)-9-(pyren-1-yl)-9H-carbazole (MePyCz).

Synthesis of 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-9-(pyren-1-yl)-9H-carbazole (MePyCz, Scheme 1)

4-(2-(2-(2-methoxy)ethoxy)ethoxy)-9H-carbazole (MeCz, 1.65 g, 5 mmol, Experimental section in ESI, Scheme S1), 1bromopyrene (1.69 g, 6 mmol), CuI (0.095 g, 0.5 mmol), 18-crown-6 (0.132 g, 0.5 mmol), and K₂CO₃ (0.76 g, 5.5 mmol) were combined with 1,2-dichlorobenzene (1.0 mL). Then the mixture was heated to 190 °C, refluxed 24 h, cooled to room temperature, washed with water, extracted with CH₂Cl₂. The organic layer was dried over MgSO₄, filtered, and concentrated in vacuum. The crude was purified by silica gel chromatography (PE/CH₂Cl₂ 4/1)to furnish the pure product of MePyCz (2.5 g, 95%). ¹H NMR (400 MH_Z, CDCl₃, ppm, Fig. S1): δ 8.55 – 8.53 (m, 1H), 8.35 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 7.6 Hz, 1H), 8.20 (s, 2H), 8.19 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.06 (t, J = 7.6 Hz, 1H), 7.94 (d, J = 9.2 Hz, 1H), 7.54 (d, J = 9.2 Hz, 1H), 7.36 - 7.30 (m, 2H), 7.25 (t, J = 8.1 Hz, 1H), 7.00 (dd, J = 6.6, 2.1 Hz, 1H), 6.78 (d, J = 7.9 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 4.53 – 4.50 (m, 2H), 4.17– 4.15 (m, 2H), 3.92 (dd, J= 5.7, 3.8 Hz, 2H), 3.82 - 3.76 (m, 2H), 3.75 - 3.70 (m, 2H), 3.61 -

3.56 (m, 2H), 3.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm, Fig. S2): δ 155.43, 143.95, 141.84, 131.44, 131.15, 130.99, 128.74, 128.61, 128.25, 127.20, 126.78, 126.67, 126.49, 125.79, 125.73, 125.51, 125.16, 124.61, 123.31, 122.74, 122.67, 120.13, 112.80, 109.65, 103.40, 101.93, 72.00, 71.04, 70.86, 70.69, 70.07, 67.74, 59.07. MALDI-TOF MS, m/z (Fig. S3): Calcd. for C₃₅H₃₁NO₄ 529.23, Found 529.62. Anal. calcd for C₃₅H₃₁NO₄: C, 79.37; H, 5.90; N, 2.64. Found: C, 79.23; H, 5.87; N, 2.65.

Synthesis of 2-(thiophen-2-yl)-fluoren-9-one (ThFO, Scheme 2)



Scheme 2. Synthesis of 2-(thiophen-2-yl)-fluoren-9-one (ThFO) by Suzuki reaction.

Typically, 2-bromo-9H-fluoren-9-one (4.0 g, 15.5 mmol), thiophen-2-ylboronic acid (5.0 g, 38.8 mmol), Pd(PPh₃)₄ (0.5 g, 0.05 mmol) were combined with the solvent of THF/toluene (25 mL/25 mL) in dark in N2 atmosphere and stirred. Then it was heated to 95°C and refluxed. After stirring for 30 min, 30 mL K₂CO₃/KF (10.764 g/4.524 g) in THF/toluene (19.5 mL/19.5 mL) was added. It should be noted that the aqueous solution of K₂CO₃/KF, THF/toluene mixed solvent should be blowed by N₂ for 2 h to eliminate oxygen. Next, the reaction mixture was stirred for 48 h, cooled to room temperature, quenched with saturated brine (50 mL) and extracted with CH₂Cl₂. The organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude was purified by column chromatography (PE/CH₂Cl₂, 4/1) to furnish ThFO as a yellow solid(3.6 g, 89%). ¹H NMR (400 MH₇, CDCl₃, ppm, Fig. S1): δ 7.91 (s, 1H), 7.74-7.67 (m, 2H), 7.52 (t, J=7.2 Hz, 3H), 7.39 (d, J = 2.8 Hz, 1H), 7.31 (t, J = 6.0 Hz, 2H), 7.11 (t, J = 5.2 Hz, 1H).¹³CNMR (100 MHz, CDCl₃, ppm, Fig. S2): δ 193.59, 144.21, 143.12, 142.96, 135.40, 134.87, 134.31, 131.53, 128.99, 128.25, 125.44, 124.40, 123.71, 121.45, 121.43, 120.76, 120.35. GC-MS (EI-m/z): 262 (M⁺). ¹³CNMR (100 MHz, CDCl₃, ppm, Fig. S2): δ 193.59, 144.21, 143.12, 142.96, 135.40, 134.87, 134.31, 131.53, 128.99, 128.25, 125.44, 124.40, 123.71, 121.45, 121.43, 120.76, 120.35. GC-MS (EI-m/z, Fig. S3): Calcd. for C₁₇H₁₀OS (M⁺) 262.05, Found 262.03. Anal. calcd for C17H10OS: C, 77.64; H, 3.84. Found: C, 77.85; H, 3.86.

Preparation of the hybrid polymer film

For the PEO/MePyCz composite, 200 mg PEO was added into 2 mL chloroform solution of MePyCz (1 mM) to get the PEO/MePyCz mixed solution (MePyCz, 0.5 wt% PEO). For the MePyCz and ThFO mixtures, different volume ratios of MePyCz/CHCl₃ (1 mM) to ThFO/CHCl₃ (10 mM) solution (v_{MePyCz} : v_{ThFO} =16:0, 16:1, 16:2, 16:4, 16:8, 0:16) were employed under a fixed amount of MePyCz of 2 mL, and then 250 mg PEO was added to get the PEO/MePyCz/ThFO composite.

For the electrospinning process, the as-prepared solution was loaded into a standard 5 mL glass syringe. The open end of the syringe was attached to a blunt stainless steel hypodermic needle (OD=0.9 mm), which was used as the nozzle. A High-Voltage DW-P403-1ACCC DC power supply was used to charge the solution by attaching the positive electrode to the nozzle and the negative grounding electrode to the aluminum collector. An electrical potential of 19 kV was applied across a distance of 15 cm between the needle tip and the collector. The electrospun solution was fed at a constant rate of 1.0 mL/ h by a syringe pump. The electrospun fiber

Journal Name

sensing films were collected on ITO glass slides mounted on aluminum foil with a collection time of 5 min.

For PEO/MePyCz spin-coating film, one drop of the above PEO/MePyCz chloroform solution with MePyCz content of 0.5 wt% was dipped onto an ITO glass slide and spin-coated at 2,000 rpm for 30s at room temperature. Then it was dried in air for 12 h.

The fluorescence quenching experiments of the sensing films towards several and other common interferents vapors are conducted as follows: a small amount of explosives (15 mg for solid or 15 μ L for liquid) was loaded in an aluminum container (5 mm×5 mm×3 mm), placed in a 1 cm×1 cm×3.5 cm quartz cell with a screw cover, and closed overnight to reach a saturation vapor pressure. The fluorescence data before and after exposure towards the analyte vapor were collected at an excitation wavelength of 330 nm at room temperature. Smoke was collected from the burning cigarette.

Characterization

¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury Plus 400M nuclear resonance spectrometer. GC-MS spectra were collected on a Shimadzu GCMS-QP 2010 spectrometer. MALDI mass spectrum was collected using a Microflex MALDI-TOF mass spectrometer (Bruker Daltonics, Germany). Elemental analyses were performed on a CHN-O-Rapid analyzer (Heraeus, Germany). FESEM images were taken on a Hitachi S-4800 field emission scanning electron microscope. Fluorescence microscope (FLM) images were taken on an Olympus IX71 (λ_{ex} =365 nm) optical microscope. UV–Vis absorption spectra were conducted at a Shimadzu UV3600-NIR recording spectrophotometer operated at resolution of 2 nm. The fluorescence spectra were conducted on a Shimadzu RF-5301 fluorescence spectrometer. The fluorescence lifetime measurements were carried out at room temperature on Edinburgh FLSP920 fluorescence spectrophotometer.

Results and discussion



Fig. 1 FESEM and FLM images of PEO/MePyCz hybrid nanofibers.

According to the FESEM image shown in Fig. 1a, the electrospun composite nanofibers of PEO/MePyCz are relatively uniform and smooth morphology with diameters ranging from 0.8 μ m to 1.6 μ m (Fig. S5). Corresponding FLM image clearly shows that the blue emitting sensing molecules of MePyCz are distributed uniformly in the PEO matrix (Fig. 1b). As shown in Fig. 2, the absorption spectrum of MePyCz in chloroform showed two individual absorption bands at 260 nm and 334 nm, which result from the higher excited state of pyrene or non-conjugated carbazole groups^{31, 32}. The emission spectra exhibited a distinct fluorescence band at 446 nm. In contrast, as for the MePyCz solid film, the absorption bands slightly red-shifted to 267 nm and 339 nm, with a new band at ca. 380 nm in the longer wavelength, whereas the emission band shifted to 463 nm, which suggests the aggregated form of pyrene and



Fig. 2 Absorbance and fluorescence spectra of (a) MePyCz in chloroform and solid film in dash and solid line, respectively ($\lambda ex=330$ nm), and (b) PEO/MePyCz nanofibers ($\lambda ex=330$ nm).

carbazole groups^{32, 33}. As for the PEO/MePyCz hybrid nanofibers, the absorption peaks located at 278, 338 nm with a new shoulder at 380 nm indicated that the existence of aggregated molecules in the composite fibers. The emission band of the fibers is at 440 nm which is similar to that in the solution state. This may be attributed to much weaker intermolecular interaction among the MePyCz molecules in the fibers than that in solid film.



Fig. 3 (a) Time-dependent fluorescence quenching process of PEO/MePyCz fibrous film towards DNT in vapor (from i to x: 0, 1, 2, 3, 4, 5, 30, 60, 90, 120 min; λ_{ex} =330 nm) (b) Time course curve of PEO/MePyCz hybrid fibrous film in ambient air without DNT. (c) Time-dependent fluorescence quenching process of PEO/PyCz fibrous film towards DNT in vapor (from i to x: 0, 1, 2, 3, 4, 5, 30, 60, 90, 120 min; λ_{ex} =330 nm). (d) The quenching efficiency curves versus exposure time with standard deviation error bars of three batches prepared at different times.

Fig. 3a shows the fluorescence spectra of PEO/MePyCz composite nanofibers towards DNT vapor. The time-dependent fluorescence quenching was measured over 2 h of exposure towards the saturated DNT vapor in air. The fluorescence of the electrospun fibrous film quenched 24% at the exposure time of 5 min (24%, Quenching efficiency, and it equals $(I_0-I)/I_0 \times 100\%$, I_0 and I are luminescence intensity of the sensor before and after exposure to the analyte), and the value reached as high as 73.2 % at 2h, which is 2.6 fold as compared with that of reported tetrakis(4-methoxylphenyl) porphyrin (TMOPP) of 28%, and besides, it should be noted that the doping content of MePyCz here is 0.5 wt%, much lower than that of TMOPP of 10 wt% to the matrix (Fig. 3a).³⁰ When the doping

further raised to 89% (Fig. S6). As seen in Fig. 3b, the fluorescence of PEO/MePyCz composite nanofibers doesn't decay a little under the excitation light in ambient air without DNT. This proves that the fluorescence quenching arises from the interaction with DNT vapor. This indicates that photo-induced electron transfer (PIET) occurred between the singlet excited state of sensor molecules and the quencher of DNT molecules in the composite nanofibers, which is in accord with their front molecular orbital energy values (Fig. S7)²⁵. Besides, the intrinsic porous structure of the electrospun nanofibers plays an important role in the high quenching efficiency of the PEO/MePyCz composite. As a comparison, the sensing performance of PEO/MePyCz spin-coating film with the MePyCz content 0.5 wt% was investigated and the quenching efficiency was much lower (58%, Fig. S8), as compared to that of electrospun nanofibers (73%, Fig. 3a). The nanofibrous film can accelerate the diffusion of DNT to encounter with MePyCz and thus benefit the detection.^{6, 25} In order to get an insight into the molecular structure effect, 9-(Pyren-1-yl)-9H-carbazole (PyCz), another compound without the alkoxy group, was synthesized from 1-bromo pyrene and 9H-carbazole by Ulmann Reaction (Experimental section in ESI, Fig. S4),³⁴ and was employed as the doped sensing matter with the same mass content with MePyCz (PyCz, 0.5 wt% PEO). The quenching efficiency of PEO/PyCz composite nanofibers towards DNT vapor in air at 5 min and 2 h were 9% and 68%, which is obviously lower than that of MePyCz of 24% and 73.2%, respectively (Fig. 3c). The LUMO and HOMO energy level of PyCz is calculated to be -1.71 and -5.15 eV, respectively, which lies in a higher position in comparison with that of MePyCz with LUMO of -2.16 eV and HOMO of -5.56 eV (Fig. S7). The electron transfer driving force from the sensing molecules of PyCz to DNT (the difference between their LUMO levels, 1.70 eV) is larger than MePyCz (1.25 eV). Therefore, PEO/MePyCz gets a definitely higher quenching efficiency with a smaller electron driving force. Swager et al. previously reported that exciton energy could migrate among the pi-conjugated polymer interchains, and Zang et al. reported there are bulky exciton diffusion along the piconjugated molecule stacked nanowires, which enables efficient fluorescence quenching by gaseous quenchers.^{25, 35} This discrepancy between the electron driving force and quenching efficiency for MePyCz and PyCz might be due to their difference in the exciton migration. There are two kinds of exciton migration ways: one is the exciton migration directly through adjacent chromophores (e.g. MePyCz), the other is the exciton migration through the donorbridge-acceptor (e.g. MePyCz-PEO-MePyCz') route. The former one have been widely exploited in the sensing system of pi-conjugated small molecule nanowires.^{25,36} The latter exciton energy migration in PEO matrix may arise from an effective tunneling through energetic bridge states barriers.³⁷ The higher quenching efficiency for MePyCz might arise from an improved exciton migration (faster speed or longer length) for MePyCz along the above two ways than PyCz.

content of MePyCz increased to 5.0 wt%, the quenching efficiency

Next, the sensing selectivity of the PEO/MePyCz is investigated towards nine substances, including *p*-NT, NB, DNT, NM, PA, naphathalene, urea, EtOH, and smoke. As seen in fluorescence quenching result in Fig. 4, the fluorescent composite nanofibers exhibit obvious quenching towards the group of nitro compounds, whereas almost no quenching was observed for the non-nitro group compounds of naphathalene, urea and EtOH. The quenching effect towards the nitro compounds is mainly due to the photoinduced electron transfer between the MePyCz molecules and the quenchers, which is in accord with the lower LUMO energy level for DNT, *p*-NT, PA, NB, NM (from DNT to NM: -3.409 eV, -3.10 eV, -4.321 eV, -2.915 eV, -2.486 eV) than that of MePyCz (-2.16 eV) (Fig. S7). In addition, we can see that the quenching efficiencies result in various degrees towards different explosives, which is not in accord



Fig. 4 Fluorescence quenching efficiencies of PEO/MePyCz electrospun nanofibrous films towards the analytes.

with the electron driving forces between MePyCz and the analyte. The quenching efficiencies of *p*-NT and NB are relatively much higher than those of three ones, which are 91.98% for *p*-NT and 85.45% for NB. This can be attributed to the difference in vapor pressure. The vapor pressure of *p*-NT was about 10^3 - fold and 10^8 - fold that of DNT and PA (200 ppm, 180 ppb, 0.0077 ppb at 25°C for *p*-NT, DNT and PA, respectively).³⁸ In comparison with *p*-NT, the relatively weak quenching observed for NB (300 ppm, 25°C) is likely due to its lower partition into the film than that of *p*-NT.^{25, 39}



Fig. 5 Absorbance and fluorescence spectra of (a) ThFO chloroform solution (λ_{ex} =440 nm) and (b) PEO/ThFO nanofibers.

Unlike the above photo-induced electron transfer (PIET) that processes in the detection of electron-deficient nitro-compounds, fluorescence resonance energy transfer (FRET) is a common energy transfer phenomenon that accompanies the exciton formation and migration and takes place between the excited state of the donor and ground state of the acceptor via intermolecular dipolar interactions.⁴⁰ It is necessary to fundamental science and industrial applications to tune the emitting color of a nanocomposite, especially based on a non-fluorescent low-cost matrix material, and study the interactions among the donor, acceptor and matrix. Herein, 2-(thiophen-2-yl)-fluoren-9-one (ThFO) serves as the energy acceptor. Its absorption spectrum showed a good overlap with the emission spectrum of MePyCz in the 400-500 nm range for its chloroform solution as well as composite polymer nanofibers with PEO (Fig. 2, 5 and Fig. S9).

Fig. 6 showed the fluorescence emission spectra of the composite nanofibers doped with MePyCz and ThFO at different ratios. With increasing the content of ThFO, the fluorescence intensity of the band at 442 nm, the characteristic emission from MePyCz, gradually decreased, and simultaneously, the 540 nm band for ThFO gradually increased. To determine the mechanism of the FRET process, fluorescence lifetime measurement of PEO/MePyCz/ThFO electrospun composite nanofibers was done. The decay of the MePyCz emission becomes faster with increasing the content of

Journal Name

ThFO (Fig. S10). This indicates that non-radiative FRET process between MePyCz and ThFO is the dominant mechanism for energy transfer.⁴¹ Corresponding fluorescence microscopy images clearly showed that the color of the nanofibers changed from blue, cyan to green for the PEO/MePyCz/ThFO composite nanofibers with different component ratios (Fig. 1b and Fig. 7a,b,c). Here, by doping 0.5 wt% small fluorophore molecule of MePyCz at most, highly fluorescent polymer nanofibers with high quantum yield of 0.29 were successfully obtained in a low-cost, large-scale and convenient way, and the color can be tuned to cyan and green by adding another simple small molecule of ThFO. To the best of our knowledge, hitherto this is the first work to control the color of polymer nanofibers by doping two small molecules between which energy transfer took place. FRET based colortuning composite materials may found potential applications in fluorescent sensors or multifunctional photoelectric devices, such as molecular sensors, biological fluorescent labels and multicolor light-emitting diodes.42,43



Fig. 6 Fluorescence spectra of PEO/MePyCz/ThFO hybrid nanofibers at different volume ratio of MePyCz and ThFO chloroform solution (v_{MePyCz} : v_{ThFO} = 16:0, 16:1, 16:2, 16:4, 16:8, 0:16) (λ_{ex} =380 nm).



Fig. 7 FLM images of (a) PEO/MePyCz/ThFO (v_{MePyCz} : v_{ThFO} =16:1), (b) PEO/MePyCz/ThFO (v_{MePyCz} : v_{ThFO} = 4:1) and (c) PEO/ThFO hybrid nanofibers.

Conclusions

Here, a new type of highly sensitive low-cost sensor towards nitro-compounds based on PEO/MePyCz (polyethylene oxide/ 4-(2-(2-(2-methoxy)ethoxy)ethoxy)-9-(pyren-1-yl)-9Hcarbazole) composite nanofibers was reported. The quenching effect arises from the photoinduced electron transfer from the fluorophores to the analytes. The much faster response and high quenching efficiency can be attributed to an improved exciton migration for MePyCz in PEO, apart from the large driving force of the electron transfer and the nanofibrous structures. apart from the large driving force of the electron transfer. Besides, it promoted an fluorescence resonance energy transfer process in the polymer fibrous matrix including a greenemitting material of 2-(thiophen-2-yl)-fluoren-9-one. The sensing composite nanofibrous film had good sensitivity and selectivity and might be constructed into a portable detector for explosives. The hybrid nanomaterials may also be applied in nano-optoelectronics devices, light-emitting diodes or biological sensors.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (21471082, 21101095, 21144004, 51173081), the National Basic Research Program of China (2012CB933301, 2012CB723402), Program for Postgraduates Research Innovation in University of Jiangsu Province (CXZZ13_0466), Scientific Research Fund Program sponsored by Nanjing University of Posts and Telecommunications (NY214128), Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD, YX03001), the Natural Science Foundation of Jiangsu Province (Grant No. BM2012010), the Ministry of Education of China (No. IRT1148), and Synergetic Innovation Center for Organic Electronics and Information Displays. The authors thank Mr. Changjin Ou, Mr. Zhengdong Liu, and Dr Lei Yang in Nanjing University of Posts and Telecommunications, and Prof. Shengbiao Li in Huazhong Normal University for their help in the synthesis of the materials.

Notes and references

1

^aKey Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China. E-mail: iamneshi@njupt.edu.cn; iamlhxie@njupt.edu.cn

^bKey Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), National Jiangsu Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, China. E-mail: wei-huang@njtech.edu.cn

†Electronic Supplementary Information (ESI) available: Synthesis part of MeCz and PyCz; ¹H NMR (400 MHz, CDCl₃, ppm), ¹³C NMR (100 MHz, CDCl₃, ppm), and MS of the compounds; The diameter distribution of the PEO/MePyCz fibers; Time-dependent fluorescence quenching process of PEO/MePyCz fibrous film with the MePyCz content of 5.0 wt%; Energy levels of HOMO and LUMO orbitals of MePyCz, PyCz and the target explosives; Time-dependent fluorescence quenching process of PEO/MePyCz spin-coating film with the MePyCz content of 0.5 wt%; FESEM images of PEO/ThFO fibers and PEO/MePyCz/ThFO hybrid fibers; Fluorescence decay profiles of PEO/MePyCz/ThFO hybrid nanofibers. See DOI: 10.1039/b000000x/

X. Lu, C. Wang and Y. Wei, Small, 2009, 5, 2349.

- 42
- P. Wang, Y. Wang and L. Tong, *Light-Sci. Appl.*, 2013, 2, 1.
 L. M. Tong, R. R. Gattass, J. B. Ashcom, S. L. He, J. Y. Lou, M. Y.
- Shen, I. Maxwell and E. Mazur, *Nature*, 2003, **426**, 816. M. Law, D. J. Sirbuly, J. C. Johnson, J. Goldberger, R. J. Savkal
- 4 M. Law, D. J. Sirbuly, J. C. Johnson, J. Goldberger, R. J. Saykally and P. D. Yang, *Science*, 004, **305**, 1269.
- 5 A. Camposeo, L. Persano and D. Pisignano, *Macromol. Mater. Eng.*, 2013, **298**, 487.
- 6 Y. Long, H. Chen, Y. Yang, H. Wang, Y. Yang, N. Li, K. Li, J. Pei and F. Liu, *Macromolecules*., 2009, **42**, 6501.
- 7 R. Yan, D. Gargas and P. Yang, *Nat. Photonics*, 2009, **3**, 569.
- 8 K. Peters, Smart. Mater. Struct., 2011, 20, 013002.
- 9 D. Li and Y. N. Xia, Adv. Mater., 2004, 16, 1151.
- L. Persano, A. Camposeo, C. Tekmen and D. Pisignano, *Macromol. Mater. Eng.*, 2013, 298, 504.
- A. Camposeo, F. Di Benedetto, R. Stabile, A. A. R. Neves, R. Cingolani and D. Pisignano, *Small*, 2009, 5, 562.
- A. Camposeo, F. Di Benedetto, R. Stabile, R. Cingolani and D. Pisignano, *Appl. Phys. Lett.*, 2007, 90.
- 13 F. Gu, H. Yu, P. Wang, Z. Yang and L. Tong, *Acs Nano*, 2010, 4, 5332.
- 14 Q. Song, L. Liu and L. Xu, J. Lightwave. Technol., 2009, 27, 4374.
- 15 F. Gu, L. Zhang, X. Yin and L. Tong, *Nano Lett.*, 2008, **8**, 2757.
- E. Holmgren, H. Carlsson, P. Goede and C. Crescenzi, *J. Chromatogr. A*, 2005, **1099**, 127.
- 17 B. Paull, C. Roux, M. Dawson and P. Doble, J. Forensic. Sci., 2004, 49, 1181.
- 18 J. M. F. Douse, J. Chromatogr., 1982, 234, 415.
- 19 M. E. Sigman and C. Y. Ma, J. Forensic. Sci., 2001, 46, 6.
- 20 R. G. Ewing, D. A. Atkinson, G. A. Eiceman and G. J. Ewing, *Talanta*, 2001, 54, 515.
- 21 J. M. Sylvia, J. A. Janni, J. D. Klein and K. M. Spencer, *Anal. Chem.*, 2000, **72**, 5834.
- 22 R. D. Luggar, M. J. Farquharson, J. A. Horrocks and R. J. Lacey, *X-ray. Spectrom.*, 1998, **27**, 87.
- 23 S. J. Toal and W. C. Trogler, J. Mater. Chem., 2006, 16, 2871.
- 24 S. W. Thomas, III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, 107, 1339.
- T. Naddo, Y. Che, W. Zhang, K. Balakrishnan, X. Yang, M. Yen, J. Zhao, J. S. Moore and L. Zang, *J. Am. Chem. Soc.*, 2007, **129**, 6978.
- 26 R. Tu, B. Liu, Z. Wang, D. Gao, F. Wang, Q. Fang and Z. Zhang, *Anal. Chem.*, 2008, **80**, 3458.
- 27 R. Li, Y. P. Yuan, L. G. Qiu, W. Zhang and J. F. Zhu, *Small*, 2012, 8, 225.
- 28 C. Zhang, Y. Che, Z. Zhang, X. Yang and L. Zang, *Chem. Commun.*, 2011, **47**, 2336.
- 29 A. Lan, K. Li, H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. Hong and J. Li, *Angew. Chem. Int. Edit.*, 2009, 48, 2334.
- 30 Y. Yang, H. Wang, K. Su, Y. Long, Z. Peng, N. Li and F. Liu, J. Mater. Chem., 2011, 21, 11895, and fig. 5d therein.
- 31 Y. Wan, L. Yan, Z. Zhao, X. Ma, Q. Guo, M. Jia, P. Lu, G. Ramos-Ortiz, J. Luis Maldonado, M. Rodriguez and A. Xia, *J. Phys. Chem. B*, 2010, **114**, 11737.
- 32 C. Zhang, Y. Che, X. Yang, B. R. Bunes and L. Zang, Chem. Commun., 2010, 46, 5560.
- 33 X. J. Zhang, X. H. Zhang, W. S. Shi, X. M. Meng, C. Lee and S. Lee, *J. Phys. Chem. B*, 2005, **109**, 18777.
- 34 S. Jeong, S. H. Park, K. S. Kim, Y. Kwon, K. R. Ha, B. D. Choi and Y. S. Han, *J. Nanosci. Nanotechno.*, 2011, **11**, 4351.
- 35 I. A. Levitsky, J. S. Kim and T. M. Swager, J. Am. Chem. Soc., 1999, 121, 1466.
- 36 Y. Che, D. E. Gross, H. Huang, D. Yang, X. Yang, E. Discekici, Z. Xue, H. Zhao, J. S. Moore and L. Zang, *J. Am. Chem. Soc.*, 2012, 134, 4978.
- 37 S. Jang, T. C. Berkelbach and D. R. Reichman, New J. Phys., 2013, 15, 105020.
- 38 G. Tang, S. S. Y. Chen, P. E. Shaw, K. Hegedus, X. Wang, P. L. Burn and P. Meredith, *Polym. Chem.*, 2011, 2, 2360.
- 39 J. S. Yang and T. M. Swager, J. Am. Chem. Soc., 1998, **120**, 11864.
- 40 N. Banerji, S. Cowan, M. Leclerc, E. Vauthey, A. J. Heeger, J. Am. Chem. Soc., 2010, **132**, 17459.
- 41 A. D. Peng, D. B. Xiao, Y. Ma, W. S. Yang and J. N. Yao, Adv. Mater., 2005, 17, 2070.

- 42 V. Vohra, U. Giovanella, R. Tubino, H. Murata and C. Botta, ACS Nano, 2011, 5, 5572.
- 43 A. Camposeo, L. Persano and D. Pisignano, *Macromol. Mater. Eng.*, 2013, 298, 487.