PAPER

Cite this: New J. Chem., 2013, 37, 1833

Received (in Montpellier, France) 27th November 2012, Accepted 30th April 2013

DOI: 10.1039/c3nj41086b

www.rsc.org/njc

Photo-induced electron transfer in a pyrenylcarbazole containing polymer–multiwalled carbon nanotube composite[†]

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A polymer incorporated with a pyrenylcarbazole pendant poly(12-(3-(pyren-1-yl)-carbazol-9-yl)dodecyl methacrylate, denoted as **PCP**) was synthesized and applied in the functionalization of multi-walled carbon nanotubes (MWCNTs) by noncovalent π - π interaction. The **PCP**-MWCNT hybrids were isolated and characterized by SEM, TEM, and UV-visible absorption and emission spectroscopies. The strong interaction between **PCP** and the MWCNT in a 1,1,2,2-tetrachloroethane (TCE) solution was studied. It demonstrated an effective quenching effect on emission from **PCP** by the MWCNTs. DFT calculations showed electron delocalization between the pyrene and carbazole moieties. The LUMO of **PCP** is mainly located on the pyrene moiety while the LUMO + 1 is predominantly positioned on the carbazole moiety. Femtosecond transient absorption (TA) experiments determined the characteristic TA peaks of the excited states, which have contributions from both the pyrene and carbazole moieties. The excited state lifetime of the polymer **PCP** was measured to be 659 ps and the photo-excited electrons were injected into the MWCNTs very effectively on a time scale of 420 fs.

Introduction

Considering the need for energy sustainability and environmental protection, solar energy is the largest carbon-neutral energy source to be explored and utilized more extensively than before.¹ The organic photovoltaic (OPV) materials and devices are envisioned to exhibit advantages such as low cost, high device flexibility, and fabrication from highly abundant materials to provide vital alternatives to their inorganic counterparts.² Most of the OPVs reported today are based on conjugated polymers as the active materials, which have been fabricated into different device architectures.³⁻⁷ The most widely studied polymer solar cell is based on solution processed bulk-heterojunction (BHJ)⁸ systems utilizing the concept of photoinduced charge transfer from a conjugated polymer donor to a fullerene acceptor.⁹ In these devices, the collection and transport of charges remains one of the most critical issues, which greatly affects the device performance. Fullerene and its derivatives

have been widely used as electron acceptors in BHJ systems and power conversion efficiencies (PCEs) as high as 6 to 7% have been achieved.¹⁰⁻¹² However, the PCE of polymer solar cells is still significantly lower (due to the extremely short exciton diffusion length¹³ in polymers) than that of their inorganic counterparts, such as Si,¹⁴⁻¹⁶ CdTe,^{17,18} and CIGS¹⁹⁻²² (copper indium gallium selenide). The use of carbon nanotube (CNT) derivatives as charge transport materials in OPV has been explored in recent years. CNTs have drawn much attention because their electronic properties make them ideal candidates for optoelectronic applications.²³⁻²⁵ The introduction of a onedimensional (1D) carbon nanotube into solar cells not only provides charge carriers with highly conductive pathways and high carrier mobility, but also offers a broad absorption band that extends into the near-infrared range due to the small energy bandgap of the CNTs.²⁶⁻³² However, the lack of solubility and the poor dispersibility of pristine CNTs in aqueous solutions arising from their strong hydrophobicity and van der Waals attractions have impeded their applications.^{33,34} Different functional groups can be introduced onto the CNT surface by covalent functionalization, which involves the chemical modification of the graphene surface of CNTs, which usually results in the degradation of the mechanical and electrical performance of the CNTs.^{35–37} Recently, we have demonstrated the functionalization of a CNT surface by a multifunctional block copolymer consisting

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/ c3nj41086b

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of a pyrene containing block and a photosensitizing ruthenium complex block. The copolymer functions as both a CNT dispersant and a photosensitizer. Upon the formation of the polymer–CNT composite, an enhancement in the photocurrent by the ruthenium complex was observed upon light irradiation.³⁸

In this paper, we report the synthesis of a polymer (PCP) functionalized with carbazole substituted units. Carbazole is a well known electron donor unit in molecules that exhibit intramolecular electronic energy transfer processes. The pyrenylcarbazole moieties in the polymer served as the anchoring units. In order to understand the fundamental photophysical processes of the polymer–CNT composite and the electronic interactions between the pyrenylcarbazole and the CNT surface, the polymer was studied by various ultrafast spectroscopic techniques. The photophysical processes regarding the charge generation and the transport dynamics were monitored by femtosecond

transient absorption (TA) spectroscopy. Our findings reveal that the pyrenylcarbazole containing polymer may act as an electron donor and CNTs may act as an electron accepting material in CNT based OPVs.

Results and discussion

Synthesis

The synthetic route of the target polymer **PCP** is shown in Scheme 1. 1-Bromopyrene was synthesized by *in situ* oxidation followed by bromination with hydrobromic acid/hydrogen peroxide.³⁹ 1-Bromopyrene was converted to the corresponding boronic ester 1 by lithiation.⁴⁰ 3-Bromocarbazole was obtained by mono-bromination of carbazole,⁴¹ and the product was subjected to an alkylation reaction by 12-bromododecan-1-ol. Monomer 4 was obtained by the subsequent nucleophilic acyl



Scheme 1 Synthesis of PCP.

substitution reaction between compound 3 and methacryloyl chloride. Methacrylic monomers are considered to be activated monomers in reversible addition-fragmentation chain transfer (RAFT) polymerization,⁴² and the chain transfer agent 5 is a commonly used dithioester that has a good control of the RAFT polymerization towards methacrylic monomers.^{43–46} Polymerization of 4 was conducted in chlorobenzene and the monomer to initiator ratio was kept at 9. From the GPC chromatogram of the polymer **PCP** obtained (Fig. S1, ESI[†]), the number average molecular weight and polydispersity were calculated to be 6470 and 1.10, respectively, which correspond to a number averaged degree of polymerization of ~8–9. This clearly shows a good molecular weight control in the RAFT polymerization.

Characterization

The ¹H NMR spectrum of **PCP** (Fig. S2, ESI[†]) shows similar spectral features as an analogous spectrum of monomer **4** but the bands are generally broadened. The broad bands from 7 ppm to 9 ppm were assigned to the protons on the pyrene and the carbazole moieties, while the peaks at *ca.* 4 to 4.5 ppm and 1 to 1.8 ppm are assigned to the protons of the methylene units. The absence of peaks from 5 to 7 ppm implies the absence of vinylene protons due to the monomer after purification.

PCP can be used as an effective dispersant for MWCNTs due to the strong π - π interaction between the pyrene moiety and MWCNTs.^{47–50} Upon mixing **PCP** and MWCNTs (10:1 wt ratio) in 1,1,2,2-tetrachloroethane (TCE) solution, most of the MWCNTs were dispersed and a black color solution was obtained. The morphology of the polymer–MWCNT composite formed was studied by TEM. The length and diameter of the commercially available MWCNTs before treatment with **PCP** are 5–20 µm and 15 nm respectively. Fig. 1a shows the TEM image of a MWCNT without **PCP** and Fig. 1b shows the TEM



Fig. 1 (a) TEM image of a pristine MWCNT. (b) TEM image of **PCP**/MWCNT obtained from TCE solution. (c) Image of MWCNTs in TCE; and **PCP**/MWCNT in TCE (1.75 mg ml⁻¹) and CHCl₃.

image of PCP-MWCNT composite obtained from the TCE solution. After dispersion with PCP, the diameter of the nanotubes obtained increases significantly due to the presence of a layer of amorphous polymeric material on the surface of the MWCNTs (Fig. 1b). The TEM image observed has an irregular surface due to the presence of the polymer, and it is easy to recognize the dense plaques around the regular MWCNT surface. Such an observation is similar to what was observed in other polymer-MWCNT composites.38 The dispersion obtained from the TCE solution has a black color, and was stable for more than one week without the formation of a precipitate. However, if the dispersion process was done in a chloroform solution, the dispersion formed was highly unstable, and the aggregates formed almost immediately (see Fig. S3 in ESI[†]). Fig. 1c shows the images of different solutions of MWCNTs and PCP/MWCNT dispersed in CHCl₃ and TCE. For the vial with chloroform solution, only a very light color solution was observed after removal of the precipitate formed. For the vial with TCE solution, the dark color persisted for a long time after dispersion, and no precipitate was observed at the bottom of the vial. The results suggest a good solvation of PCP/MWCNT in TCE, which formed a stable dispersion. The stability of the dispersion may be due to the stronger solvent-polymer-MWCNT interactions, but the reason is not clear. In view of the stability of the solution, all the measurements on the photophysical properties were conducted in TCE solution.

Fig. 2a shows the UV-vis absorption spectra of PCP and PCP/ MWCNT in different solvents. Pyrene shows intense absorption peaks at 340 and 275 nm, and carbazole shows strong absorption at ca. 290 nm and weaker absorption bands at 310-320 and 330–350 nm.^{51–54} In the absorption spectrum of **PCP**, the peaks at 269, 280 and 350 nm are assigned to the absorption due to the pyrene and carbazole moieties, and some of the weaker absorptions are observed as shoulders. On the other hand, the absorption spectrum of PCP/MWCNT in TCE is dominated by the characteristic absorption of the MWCNTs, which displays a very broad and intense absorption in the range between 300 nm and 800 nm.⁵⁵⁻⁵⁷ Nevertheless, the absorption due to the pyrene and carbazole moieties can still be identified by the presence of a peak and a shoulder at ca. 270 and 370 nm, respectively. The shift in the absorption baseline for PCP/MWCNT in TCE indicates the rich presence of MWCNTs in the solution, and may also be contributed from undispersed MWCNTs.

The thermal stability of the polymers and composites was investigated by thermal gravimetric analysis (TGA) under a nitrogen atmosphere. In the TGA thermograms shown (Fig. 2b), pristine MWCNTs have an initial decomposition temperature at 550 °C, while the onset of decomposition of **PCP** is observed at 400 °C and it completely decomposes at 500 °C with almost no residue left. The weight loss below 400 °C may be due to the evaporation of residual solvents. For the **PCP**-MWCNT composite, the initial decomposition temperature is the same as **PCP**, but a weight residue of 20% was obtained at 700 °C. From these data, it can be estimated that the content of **PCP** in the composite **PCP**-MWCNT is approximately 75%.



Fig. 2 (a) UV-vis absorption spectra of **PCP** (0.025 mg ml⁻¹) and **PCP**/MWCNT (MWCNTs 0.02 mg ml⁻¹) in TCE solutions. (b) TGA analysis of MWCNTs, **PCP**, and **PCP**/MWCNT respectively, under a nitrogen atmosphere, with a speed of 10 °C per min.

Fluorescence quenching effects

Fig. 3 shows the fluorescence spectra of PCP and PCP/MWCNT collected in TCE solutions. The fluorescence spectra of pure pyrene, carbazole and compound 3 are also shown for comparison. Both pyrene and carbazole show very strong emission bands at ca. 380-400 and 320-370 nm, respectively. 58,59 PCP shows one single broad emission band centered at 430 nm, which is substantially red-shifted compared to those of carbazole and pyrene. The emission spectrum of PCP is similar to that of compound 3 in both dilute and concentrated solutions, which suggests that the pyrene moieties in PCP do not form excimers. The sharp emission bands from pyrene or carbazole moieties are not observed in the emission spectrum of PCP. This may be due to the conformational change of the pyrene and carbazole units in PCP. After forming the PCP-MWCNT composite, the emission was almost completely quenched compared to that from PCP (Fig. 3, bottom). This suggests the presence of a strong electronic interaction between the excited state of PCP and MWCNTs.

DFT calculations

The electronic structures of **PCP** were studied by DFT calculations, which were performed at the B3LYP/6-311G** level of theory for the



Fig. 3 Emission spectra of (a) pyrene and carbazole; (b) PCP, PCP/MWCNT, and compound 3 in 1,1,2,2-tetrachloroethane (excitation wavelength = 266 nm).

geometry optimization and vibrational frequency calculations. Only the 12-acetyloxydodecyl substituted pyrenylcarbazole segment in PCP was used as the model compound in the calculation to estimate the electronic energy levels and electron density, because this is the unit that interacts strongly with the MWCNT. Fig. 4 shows the frontier orbitals and energy levels of the 12-acetoxydodecyl pyrenylcarbazole unit obtained from the DFT calculations. The standard orientation of the unit is presented in Table S1 (ESI⁺). As expected, the long acetyloxydodecyl chain has no contribution to the frontier orbitals HOMO, LUMO and LUMO + 1 in the molecule. The HOMO is located both on the pyrene and carbazole units. It can be seen that the pyrene and carbazole rings form a dihedral angle of 60° and they have some degree of conjugation in the HOMO electron distribution. On the other hand, the LUMO is mainly located on the pyrene unit, while the LUMO + 1 is predominantly on the carbazole unit. This may partially explain in Fig. 3 that the emission band of PCP is similar to that of pyrene, while the emission features of carbazole are not observed.

Electrochemical properties

The electrochemical properties of **PCP** were studied by cyclic voltammetry (CV), and its HOMO and LUMO levels were



Fig. 4 Frontier orbitals (left) and energy levels (right) of pyrenylcarbazole model compound obtained from the DFT calculations.

estimated by comparing the redox potential observed with that of ferrocene acting as the internal standard. The cyclic voltammogram is shown in Fig. 5. The onset oxidation potential (0.52 V) was used to estimate the HOMO level of **PCP**, which was calculated by comparing this potential with the ferrocene/ferrocenium (Fc/Fc⁺) couple using the relationship: $E_{\text{HOMO}} = -(E_{\text{oxi}}^{\text{onset}} + 4.8)^{60}$ and $E_{\text{LUMO}} = E_{\text{HOMO}} + \text{Optical Band}$ Gap.⁶¹ The optical bandgap was estimated from the absorption band edge of **PCP**. Two irreversible anodic waves at 0.8 and 1.4 V are observed, which are assigned to the oxidation of the pyrenylcarbazole units. Table 1 summarizes the HOMO/LUMO

levels of **PCP** obtained by CV and by DFT calculations. In general, the experimental and theoretical results agree very well with each other, except that the LUMO level obtained by the DFT calculations is higher than that obtained from CV. This discrepancy may be attributed to the fact that when calculating the HOMO-LUMO gap directly from the optical bandgap, factors such as Coulomb and exchange integral between HOMO and LUMO are not taken into account. In addition, in the calculations where only one repeating unit of **PCP** was involved, some approximations in the DFT calculations, such as Coulombic and exchange interactions, and vibronic coupling, have also been adopted.^{5,62}



Fig. 5 Cyclic voltammogram of PCP.

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	LUMO level (eV)	HOMO level (eV)	Bandgap (eV)
DFT	-1.69	-5.29	3.60
CV and $E_{\rm op}$	-2.15	-5.32	3.17

Compared with our previously reported pyrene-containing polymer, **PCP** has a higher HOMO level (-5.32 vs. -5.83 eV),³⁸ which may be due to the presence of a partially conjugated system. The conjugation also results in a smaller bandgap of **PCP** (3.17 eV) than that of poly(*N*-vinylcarbazole) (3.53 eV).⁶³

Transient absorption spectroscopy and electron transfer kinetics

Fig. 6 shows the temporal evolution of the femtosecond TA spectra for **PCP** and **PCP–MWCNT**. The TA spectra of pyrene, carbazole, and pure TCE are also shown for comparison. In Fig. 6a, pyrene shows two strong TA peaks at 370 nm and 480 nm and with a weak shoulder at *ca.* 520 nm. This is consistent with the literature reported spectra.⁶⁴ Carbazole shows a strong and broad TA band centered at 625 nm. From Fig. 6b, it can be seen that pure TCE solvent demonstrates no TA band in the region between 500–650 nm, which has no overlap with the region which we studied. In Fig. 6c, **PCP** shows



Fig. 6 (a) Femtosecond TA spectra of pyrene and carbazole. (b) Femtosecond TA spectra of pure TCE. (c) and (d) Temporal evolution of TA spectra for PCP. (e) and (f) Temporal evolution of TA spectra for PCP/MWCNT. All measurements were done in 1,1,2,2-tetrachloroethane solutions and the excitation wavelength was 266 nm.

the growth of a strong and broad TA band centered at 610 nm and a negative TA band centered at 430 nm. By comparing Fig. 6a and c, the TA band at 610 nm may be assigned to the contribution from the carbazole moieties in PCP. The negative TA band at 430 nm may be due to the induced emission of PCP. A shoulder is also noticed at 490 nm in Fig. 6c. It grows to a maximum at 1.9 ps and disappears rapidly within 30 ps. The shoulder at 490 nm may be due to some intermediate states between the higher excited state and the final longer living S1 state, which is supported by the observation of an isosbestic point between the absorption of this intermediate and the S1 state at 520 nm. This intermediate is not observed in the TA decay profile of PCP in Fig. 6d. Fig. 6e and f show the TA growth and decay profile of the PCP-MWCNT composite. The disordered spectra before 500 nm are assigned to the temporal evolution of TA spectra of TCE, which agrees well with the spectra shown in Fig. 6b. In Fig. 6e and f, only the characteristic bands due to the carbazole moieties are observed, while the TA bands due to the pyrene units are not detected. Besides, in the TA spectra of PCP/MWCNT, no negative band of emission is observed. This result suggests that the excited state of the pyrene unit does not undergo decay through emission. Instead, electrons may be transferred to the MWCNT and such an electron transfer process is too rapid to be detected on the femtosecond time scale. By comparing Fig. 6d and f, it can be seen that the TA decay of PCP is three orders of magnitude more rapid in the presence of the MWCNT. The decay process of PCP lasts for approximately 3 ns, while for PCP/MWCNT it is only 3 ps. This strongly suggests that there is a rapid electron transfer from the carbazole localized excited state to the MWCNT.

The electron transfer from the excited states of **PCP** to the MWCNT may be explored by the TA kinetics. Fig. 7 shows the TA kinetics of **PCP** and **PCP/MWCNT** in both a longer and a shorter time window. From Fig. 7a, the TA of **PCP** has a slow decay profile and it does not decay to zero within 2000 ps, while for **PCP/MWCNT**, the TA decays very fast and it cannot be observed precisely in the longer time window. From Fig. 7b, it can be seen that the TA of **PCP/MWCNT** decays completely in less than 5 ps. These TA kinetics are both fitted well by multi-exponential functions that include growth and decay processes. The multi-exponential function used is defined to be

$$I = A_{g} \exp(-t/\tau_{g}) + A_{d1} \exp(-t/\tau_{d1}) + A_{d2} \exp(-t/\tau_{d2})$$

where *I*, *A*, *t*, τ_g , τ_d represent TA intensity, constants, decay time, time constant for the growth process, and time constant for the decay process, respectively. The lifetime of the excited state τ is defined by

$$\tau = \tau_{d1} [A_{d1} / (A_{d1} + A_{d2})] + \tau_{d2} [A_{d2} / (A_{d1} + A_{d2})].$$

The electron injection process from excited **PCP** to the MWCNTs may be quantified by the half-lifetimes ($\tau_{1/2}$), which is defined as the time when the amplitude of the decay curve decreases to half of the initial value.⁶⁵ The fitting results are summarized in Table 2. The lifetime of the excited state of **PCP** is 659 ps, which is much longer than the electron injection time



Fig. 7 (a) TA kinetics of PCP and PCP/MWCNT in 1,1,2,2-tetrachloroethane solutions, (b) the same profiles in a shorter period. Wavelength of the pump beam = 266 nm (power = 30 mW), wavelength of the probe beam = 610 nm.

 $\label{eq:Table 2} \mbox{ Fitting results of TA kinetics for PCP and $PCP/MWCNT$ calculated from $Fig. 7$}$

Time constant	$\tau_{\rm g} ({\rm ps})$	τ_{d1} (ps)	$\tau_{d2} \ (ps)$	τ (ps)	$\tau_{1/2} (ps)$
PCP	7.78	108	992	659	
PCP/MWCNT	—	0.40	16.2	—	0.42

from excited **PCP** to the MWCNTs (0.42 ps). The time constant of the TA growth process for **PCP**/MWCNT is too short to be calculated due to a rapid decay, while for **PCP** it is calculated to be 7.8 ps. This suggests that the electron transfer to the MWCNTs may occur from a higher excited state of **PCP** before relaxation to the S1 state, since the S1 state has a longer growing time than the electron injection time (7.8 ps *vs.* 0.42 ps).

Conclusions

A pyrenylcarbazole containing polymer (**PCP**) was synthesized and used as the dispersing agent for MWCNTs. The polymer could disperse MWCNTs efficiently by the formation of π - π stacking between the pyrenylcarbazole and the MWCNTs surface

in a TCE solution. DFT calculations showed that the HOMO of the polymer spreads around the whole aromatic ring, while the LUMO and LUMO + 1 of the polymer are mainly located on the pyrene and carbazole units, respectively. Femtosecond transient absorption (TA) spectra demonstrate the characteristic TA peaks of excited states of PCP contributed from the pyrene and the carbazole moieties. In the PCP-MWCNT hybrids, the excited state electrons are rapidly transferred to the MWCNTs, and the fluorescence of PCP was effectively quenched. The lifetime of the excited state of PCP is 659 ps and the electron injection time to the MWCNTs is 420 fs. Based on the results obtained in this work, it is possible to design new polymeric materials such as block copolymers for light harvesting applications. Other light harvesting units may be incorporated into a PCP main chain, and the resulting materials may serve as potential candidates for photosensitizers and electron acceptors in polymer solar cells.

Experimental section

The synthetic procedures for making the monomer 4, the chain transfer agent 5, and other intermediates are described in ESI.[†]

Synthesis of poly(12-(3-(pyren-1-yl)-9*H*-carbazol-9-yl)dodecyl methacrylate) (PCP)

Monomer 4 (0.592 g, 0.955 mmol), 2-cyanoprop-2-yl dithiobenzoate 5 (0.021 g, 0.106 mmol) and AIBN (8 mg, 0.0053 mmol) were dissolved in chlorobenzene (2.3 ml) in a 10 cm³ ampoule under a nitrogen atmosphere. The solution was degassed by three freeze–pump–thaw cycles and sealed under vacuum. The mixture was heated at 60 °C in the dark for 24 hours. The crude product was precipitated in methanol (250 cm³) and the solid was obtained by filtration. The solid was re-dissolved in a minimum amount of chloroform and reprecipitated in methanol again. The precipitation procedure was repeated twice. The purified polymer was dried under vacuum and appeared as a pink solid. Yield: 0.491 g (80%).

Preparation of the PCP-MWCNT composite

MWCNTs (0.5 mg) and **PCP** (10 mg) were dispersed in 6 ml of solvent (TCE or chloroform), and the mixture was ultrasonicated for 1 h at room temperature. The sediment was removed by a filter paper and the light black sediment on the filter paper was mainly undispersed MWCNTs which were discarded. The resulting solution obtained was filtered using a PTFE membrane filter (0.2 μ m) to remove any excess polymer from solution. The **PCP**/MWCNT remaining on the surface of the membrane filter was then redispersed in TCE solution by ultrasonication. The resulting **PCP**/MWCNT dispersion in TCE was stable at room temperature for more than one week.

Measurements

UV-vis absorption spectra were collected on a U-2910 spectrometer (Hitachi, Japan). Fluorescence spectra were collected on an F-7000 fluorescence spectrophotometer (Hitachi, Japan). SEM images were collected using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800) and TEM images were collected using a Philips Tecnai G2 20 S-TWIN scanning transmission electron microscope. Samples for TEM were prepared by dispersing the composite in TCE onto a carboncoated 400-mesh hexagonal copper grid at room temperature. TGA thermograms were collected using a thermogravimetric analyzer (NETZSCH STA 449F3) under a nitrogen atmosphere at a heating rate of 10 °C per min. Cyclic voltammetry was performed on an eDAQ EA161 potentiostat. A 3 mm glassy carbon electrode was used as the working electrode, a platinum foil was used as the reference electrode and a platinum wire was used as the auxiliary electrode. 0.1 M tetrabutylammonium hexafluorophosphate and deoxygenated HPLC grade dichloromethane was used as the supporting electrolyte and solvent, respectively.

DFT calculations

The geometry optimization, vibrational frequency and DFT calculations were done using the B3LYP method with a 6-311G** basis set for the singlet state. All of the density functional theory calculations presented in this work made use of the Gaussian 03 program suite⁶⁶ installed on the High Performance Computing cluster at Computer Centre in The University of Hong Kong.

Transient absorption measurements

The femtosecond TA experiment was carried out using a femtosecond Ti:sapphire regenerative amplified Ti:sapphire laser system (Spectra Physics, Spitfire-Pro) and an automated data acquisition system (Ultrafast Systems, Helios). The pump laser was of 267 nm (the third harmonic of the fundamental 800 nm from the regenerative amplifier). The probe pulse was a white-light continuum (300–800 nm) generated by a CaF₂ crystal using approximately 5% of the original output from the Spitfire. Before passing through the sample the probe pulse was split into two beams: one beam travels through the sample, and the other is sent directly to the reference spectrometer that monitors the fluctuation of the probe beam intensity. The instrument response function is evaluated to be 150 fs. The signals of all samples TA experiments were reproducible, and therefore the accumulation of photo-catalytic products was negligible.

Acknowledgements

The work described in this paper was substantially supported by the University Grants Committee of the Hong Kong Special Administrative Region, China (Project No. T23-713/11, HKU 7039/07P, HKU 7003/11P, N_HKU705/10, Special Equipment Grant SEG-HKU-07). J. Xi acknowledged the support from the National Natural Science Foundation of China (20973099).

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