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Conjugated copolymer-photosensitizer molecular hybrids with broadband visible light absorption for efficient light-harvesting and enhanced singlet oxygen generation[†]

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We have developed conjugated copolymer-photosensitizer molecular hybrids (PFBDBP-IPBP) with a strong, broad (from <400 nm to \sim 700 nm) and continuous visible absorption. The photosensitizing ability of PFBDBP-IPBP was demonstrated to be higher than that of the monochromophore-based IPBP, owing to rational manipulation of the multiple intramolecular energy transfer. In addition, we demonstrated that the developed PFBDBP-IPBP displays excellent photostability compared to the IPBP.

Light-induced generation of singlet oxygen (${}^{1}O_{2}$) from triplet photosensitizers has been a reaction of widespread interest.^{1,2} To date, there are many reported or commercially available photosensitizers, but these triplet photosensitizers alone intrinsically suffer from either low molar absorption coefficient in the visible spectral region and/or narrow light absorption band.^{1–5} Much work on achieving broadband visible light absorption has come from the construction of multi-chromophore based small molecular hybrids capable of efficient energy transfer between two or more light-absorbing components, but there is still an appreciable visible spectrum (400–700 nm) unable to be efficiently absorbed.^{6–11}

Fluorescent conjugated polymers have been frequently exploited as energy donors for enhancing the light-harvesting efficiency of photosensitizers, which are well-known to have advantages of large molar absorption coefficient, excellent photostability, and high brightness.¹²⁻¹⁸ However, although to some extent these hybrid photosensitizers are capable of extending the range of the light-harvesting spectrum, still only a part of the visible spectrum can be successfully covered.^{19–24} To our knowledge, it still remains a significant challenge to develop multi-chromophore based photosensitizers with

greatest spectral cross-sections of the visible spectrum (*i.e.*, with as broad absorption bands in 400–700 nm as possible), at least partially owing to the spectroscopic limitation of the light-absorbing components required to meet the Förster theory as well as the lack of potent energy donor chromophores with continuous visible light absorption bands.

In this work, we report the design and synthesis of multichromophore based molecular hybrids (PFBDBP-IPBP) containing a fluorescent conjugated copolymer backbone PFBDBP and a covalently linked photosensitizer IPBP (Scheme 1 and ESI[†]), which show extremely broad absorption bands (from <400 nm to \sim 700 nm) in the visible region and a high efficiency of ¹O₂ generation under visible wavelength excitation. The detailed synthetic route is provided in Scheme S1 in the ESI.† Two chromophores that, upon conjugation with fluorene monomer units via Suzuki polymerization, absorb light in the wavelength range of 400-550 nm and 500-600 nm, respectively, (Fig. S1[†]) were exploited for the design of the conjugated copolymer backbones. That is, a 2,1,3-benzoxadiazole-based monomer (BD) and a BODIPY-based monomer (BP), which also show strong fluorescence emission in the wavelength range of 500-700 nm (PFBD) and 550-700 nm (PFBP), respectively, after polymerization (Fig. S1[†]).²⁵⁻³⁰ The polymers were branched with iodinated BODIPY chromophores, which have been a unique



Scheme 1 Illustration of the molecular design and chemical structure of PFBDBP–IPBP.

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class of photosensitizers, owing to their large absorption coefficient, good photostability, and high triplet state quantum yield.^{31–34} In our system, **IPBP**, an iodinated BODIPY shows a major absorption band in the wavelength range of 550–700 nm (Scheme 1 and Fig. 1), which has a broad overlap with the emission spectrum of **PFBD** and **PFBP**. Thus the **IPBP** was expected to serve as the energy acceptor and a triplet photosensitizer chromophore (Fig. S1†). Potential advantages of the developed molecular hybrids relative to photosensitizers alone (or other existing hybrids in the literature) not only lie in their super-strong visible light-harvesting ability, but also include the flexibility of hybrid components (*i.e.*, the ability of being postmodified, and fluorescence imaging capability).^{21,35}

In the final construction, BD and BP were incorporated in a ratio of 7/3 with azide-appended fluorene monomers as the bridges to generate the conjugated copolymer PFBDBP; after that, 6% molar **IPBP** (molar ratio of [**IPBP**]/[azide-group]) photosensitizer was conjugated covalently to the backbones through an efficient click reaction to generate the final molecular hybrids, **PFBDBP–IPBP**. The molecular weight (M_n) of **PFBDBP** was measured to be 23 766 with a M_w/M_n of 1.94 as determined by GPC. Each polymer contains an average of \sim 80 repeating azide-group units. Thus, the broadband visible lightinduced capability was achieved through energy transfer from either BD or BP units in the backbone to the side-chain IPBP photosensitizers and/or through a multi-step transfer of energy from BD to BP units. The energy transfer from PFBDBP to IPBP contributes significantly to the enhancement of the efficiency of singlet oxygen generation.

As shown in Fig. 1, **PFBDBP** exhibits two major absorption bands in the visible spectrum of 400–500 nm and 500–600 nm. The molar absorption coefficient of **PFBDBP** at the two absorption peaks (445 nm and 545 nm) can be estimated to be $1.80 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ and $2.64 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ (in polymer backbone units), respectively. We further found that **PFBDBP** has relatively high absolute photoluminescence quantum yield; that is, 40.7% and 37.1%, when excited at 445 and 545 nm, respectively. Accordingly, the copolymer **PFBDBP** that has broad absorption bands in the wavelength range of 400–600 nm is highly fluorescent upon excitation at visible wavelengths. Moreover, the fluorescence emission of **PFBDBP** has a very broad overlap with the absorption of **IPBP** (Fig. 1), thus enabling





Fig. 2 Normalized UV-Vis absorption spectra of PFBDBP–IPBP, PFBDBP and IPBP. The concentration of PFBDBP (in PFBDBP units), PFBDBP–IPBP (in PFBDBP units) and IPBP is 2.0×10^{-6} M. Solvent: DCM.



Fig. 3 Fluorescence emission spectra of **PFBDBP** and **PFBDBP–IPBP**: (a) $\lambda_{ex} = 445$ nm and (b) $\lambda_{ex} = 545$ nm excitation wavelength (5.0 \times 10⁻⁸ M, in **PFBDBP** unit). Solvent: DCM.

efficient intramolecular energy transfer, which leads to fluorescence quenching of the copolymers (energy donor). Fig. 2 shows that PFBDBP-IPBP has extremely broad absorption bands (from <400 to \sim 700 nm) in the visible region, which can improve the utilization of the visible light. Fig. 3 shows that the fluorescence of PFBDBP was significantly quenched in PFBDBP-IPBP by 96% and 95% when excited at 445 nm and 545 nm, respectively. Furthermore, the luminescence lifetime of the residual PFBDBP compared to the free PFBDBP was used to evaluate the intramolecular energy transfer efficiency between PFBDBP and IPBP. When excited at 457 and 566 nm, the lifetime of PFBDBP reduced from 3.79 and 3.80 ns to 1.99 and 2.18 ns (Fig. 4), which implies an energy transfer efficiency (ET) of 47% and 43%, respectively.^{6,36} It is worth noting that the efficiency of ET was much less than the quenching efficiency. We proposed that the inefficient intramolecular energy transfer is likely due to the intramolecular electron transfer.36,37



Fig. 4 Emission decay curves of PFBDBP and PFBDBP–IPBP: (a) $\lambda_{ex} =$ 457 nm and (b) $\lambda_{ex} =$ 566 nm. Solvent: DCM.



Fig. 5 Plots of $ln(C_t/C_0)$ vs. irradiation time for the photooxidation of DHN using different triplet photosensitizers. [Photosensitizers] = 2.0×10^{-6} M (in IPBP units), [DHN] = 1.0×10^{-4} M, 20 °C. Solvent: DCM/MeOH (9/1, v/v), 20 °C.

In order to evaluate the efficiency of the strong, broad and continuous absorbing triplet photosensitizers, it is interesting to explore their utility as photooxygenation catalysts to produce singlet oxygen $({}^{1}O_{2})$. Therefore, as a representative example, 1,5dihydroxynaphthalene (DHN) was used as the singlet oxygen (¹O₂) scavenger which produces juglone upon oxidation.³⁸ Upon excitation with a panchromatic xenon lamp, the absorption of DHN at 301 nm decreased due to the oxidation by ¹O₂ produced from the triplet photosensitizer. Meanwhile, the absorption of the product (juglone) at 427 nm increased (Fig. S2[†]). No obvious change in the absorption spectrum of the triplet photosensitizers was observed, indicating the excellent photostability of the triplet photosensitizers under these excitation conditions (Fig. S2[†]). Photooxidation of DHN with PFBDBP-IPBP and IPBP can be quantitatively evaluated by plotting $\ln(C_t/C_0)$ against the irradiation time (Fig. 5). Oxidation rate constants (OCR) can be derived from the slope of these curves. The results showed that, at the same concentration of the IPBP unit, the OCR of **PFBDBP-IPBP** is 0.077 min⁻¹, a value which is much higher than that of IPBP (0.049 min^{-1}). Thus we demonstrated that the strong, broad and continuous absorption of PFBDBP-IPBP significantly improves the triplet photosensitizing efficiency. Notably, both PFBDBP-IPBP and IPBP were more efficient than the conventional triplet photosensitizers such as tetraphenylporphyrin (TPP, 0.033 min⁻¹) and methylene blue (MB, 0.014 \min^{-1}) (Fig. 5).³⁹

Furthermore, in order to study the effect of the intramolecular energy transfer on the photooxidation efficiency, the



Fig. 6 Comparative singlet oxygen $({}^{1}O_{2})$ generation experiment. Absorbance decrease of DPBF with time in the presence of different triplet photosensitizers. Photoexcitation at (a) 445 nm and (b) 545 nm. [Photosensitizers] = 2.5×10^{-6} M (in IPBP units), 20 °C. Solvent: DCM.



Fig. 7 Photobleaching of IPBP (a) and PFBDBP–IPBP (b) under continuous irradiation. [Photosensitizers] = 1.0×10^{-5} M (in IPBP units), 20 °C. Solvent: DCM.

photosensitizing ability of the photosensitizers was studied with monochromatic light excitation at the absorption band of the energy donors **BD** unit, **BP** unit and energy acceptor **IPBP**, respectively. 1,3-Diphenylisobenzofuran (DPBF) was used as the singlet oxygen scavenger.⁴⁰ Upon excitation at 445 and 545 nm, the photosensitizing activity of **PFBDBP–IPBP** is higher than that of **IPBP** (Fig. 6). These results demonstrated the effect of intramolecular energy transfer in **PFBDBP–IPBP**. Hence the performance of branched conjugated copolymer triplet photosensitizers is enhanced by the intramolecular energy transfer effect, in which a strong, broad and continuous absorption in the visible region has been achieved.

In addition, owing to the excellent photostability of conjugated polymers, degradation of **PFBDBP-IPBP** under a strong and continuous light excitation can be significantly reduced. The result of the photobleaching experiment shows that, after 60 minutes of continuous irradiation with strong light, the degradation of **IPBP** was 20.5% (Fig. 7a). In contrast, only 4.1% of **IPBP** was degraded while **IPBP** was grafted to the polymer (Fig. 7b). The impressive five-fold enhancement of photostability highlights the significance of protection afforded by the conjugated polymer backbone.

In conclusion, we have developed branched photosensitizer triplet photosensitizers **PFBDBP-IPBP** with a strong, broad (from <400 nm to ~700 nm) and continuous visible absorption. Their photosensitizing ability was relatively higher as compared with the monochromophore-based **IPBP**, owing to the multiple intramolecular energy transfer. Besides, **PFBDBP-IPBP** shows excellent photostability. Our results demonstrated a new method to design efficient and environmentally friendly triplet photosensitizers, and the feasibility of exploiting them in a wide range of areas.

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