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White-light emitting dye micelles in aqueous solution†

Cite this: DOI: 10.1039/c3cc44875d

Xin Zhang, Daniel Görl and Frank Würthner*

Received 29th June 2013,
Accepted 26th July 2013

DOI: 10.1039/c3cc44875d

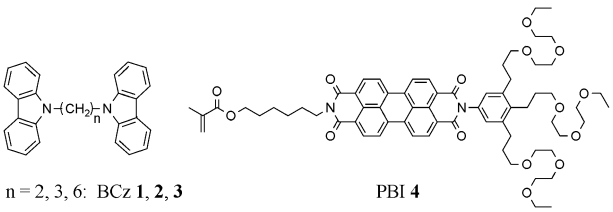
www.rsc.org/chemcomm

Biscarbazole-loaded perylene bisimide (PBI) dye micelles in water afforded a fluorescence resonance energy transfer (FRET)-based white-light emitting nano luminary system with biscarbazoles as energy donors and PBI micelles as acceptors.

Water-soluble luminescent assemblies of organic building blocks have attracted much attention because of their potential applications as fluorescence sensors and probes in biological systems, and as energy collecting and transfer materials for artificial photosynthesis.[1,2] Among such luminescent assemblies, white-light emitting systems are of particular interest for a wide range of applications.[3] On the basis of the Commission Internationale de l'Eclairage (CIE) chromaticity diagram, white light can be achieved by careful tuning of each colour contribution[4] and energy transfer between dye components in an assembling system.[5] In the past years, various organic composites have been reported that emit white light in thin-films,[6–11] organogels,[12] and vesicles.[13,14]

For a few years, one of our research interests has been self-assembly of perylene bisimide (PBI) dyes in water.[15] Previously, we reported on the precise control of morphology of PBI dye aggregates to obtain nanorods, bilayer vesicles and spherical micelles in water.[16] Moreover, we developed luminescent vesicular nanocapsules of 30–40 nm diameter based on PBI dyes which displayed pH-dependent emissive colours including white light.[14] In this work, we report on functionalization of much smaller nanosystems of <10 nm diameter, *i.e.* PBI dye micelles, by loading biscarbazoles with appropriate spacer length into the micelle interior to obtain nano-sized fluorescence resonance energy transfer (FRET) systems. To the best of our knowledge, we demonstrate here for the first time white-light emitting dye micelles that are created from molecular building blocks in aqueous solution.

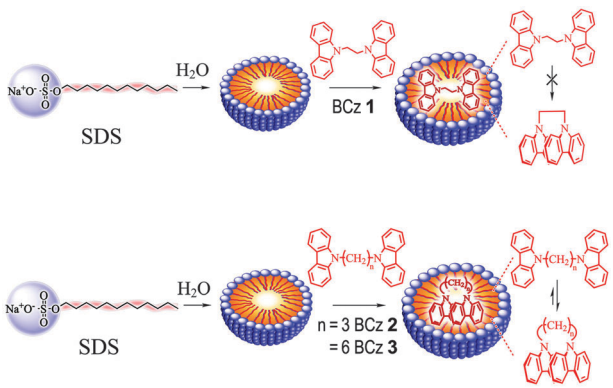
We have employed biscarbazoles (BCzs) **1–3** (Scheme 1, for the synthesis and characterization see ESI†) with varied spacer lengths[17] as energy donor molecules and amphiphilic PBI **4** (ref. 16) as an energy acceptor building block in the exterior of morphologically distinct micelles created by self-assembly in water.



Scheme 1 Chemical structures of BCzs **1**, **2**, **3**, and PBI **4**.

Prior to the investigations employing PBI micelles, we first studied loading of BCzs into a model micelle system using the well-known surfactant sodium dodecyl sulfate (SDS), which readily forms micelles in water (Scheme 2, for details see ESI†).[18] Since the micelle interior is highly hydrophobic,[18] hydrophobic biscarbazoles are adsorbed into the hydrophobic interior of SDS micelles in aqueous solution (Scheme 2) as confirmed by fluorescence spectroscopy (Fig. 1b and Fig. S5, ESI†).

Our choice of α,ω-alkyl tether-linked biscarbazoles was based on earlier work by De Schryver and coworkers who showed that



Scheme 2 Schematic illustration of the loading of BCz **1**, **2** or **3** into sodium dodecyl sulfate (SDS) micelles in aqueous solution.

Universität Würzburg, Institut für Organische Chemie and Center for Nanosystems Chemistry, Am Hubland, 97074 Würzburg, Germany.
E-mail: wuerthner@chemie.uni-wuerzburg.de

† Electronic supplementary information (ESI) available: Synthetic details, additional NMR, UV/vis, fluorescence and TEM data. See DOI: 10.1039/c3cc44875d

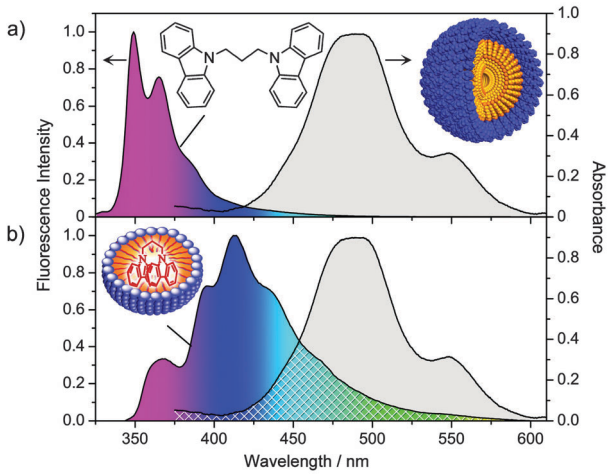


Fig. 1 (a) Fluorescence spectrum of BCz **2** in THF and UV-vis absorption spectrum of PBI **4** micelles in aqueous solution; [BCz **2**] = 5.0×10^{-6} M, [PBI **4**] = 2.86×10^{-5} M. (b) Fluorescence spectrum of BCz **2**-loaded SDS micelles in aqueous solution and UV-vis absorption spectrum of PBI **4** micelles in aqueous solution; [BCz **2**] = 5.0×10^{-6} M.

these molecules prevail in different conformations depending on the respective alkyl chain length and the solvent.[17] In particular for 1,3-di-*N*-carbazolylpropanes, *e.g.* BCz **2**, which are model systems for the first commercial organic photoconductor poly(*N*-vinylcarbazole), it was shown that stacked conformations are preferred over extended ones in low polarity environments.[17] While in the extended conformation two carbazole rings stretch outward as observed in the polar solvent THF for BCz **2** (Fig. 1a), in stacked conformations two carbazole rings are packed face-to-face by intramolecular π–π-stacking interaction, leading to intramolecular excimer fluorescence as observed in aliphatic solvents,[17] or in the interior of SDS micelles as shown in Fig. 1b.

UV-vis absorption spectra of BCz **2** are concentration-independent, which further confirms the intramolecular stacking of BCz **2** (Fig. S4, ESI†). The fluorescence spectra display a large spectral shift from the UV (320–400 nm, Fig. 1a) in good-solvating THF solvent to visible cyan-blue (380–550 nm, Fig. 1b) in the low-polarity interior of SDS micelles. For BCz **3**, quite similar to BCz **2**, the intramolecularly stacked conformation is predominant in the confined interior space of SDS micelles according to fluorescence spectra (Fig. S5b, ESI†). In contrast, for BCz **1**, only the extended conformation exists in solution as well as in the low-polarity confined interior space of SDS micelles as revealed by fluorescence spectroscopy (Fig. S5a, ESI†). Thus, within SDS micelles, BCz **1** displays two fluorescence peaks at 335 nm and 360 nm similarly to those observed in good-solvating solvents for aromatic π-systems such as THF. This finding is quite reasonable since the ethylene spacer between two carbazole rings of **1** is too short, and thus intramolecular stacking is disfavoured due to the geometrical restriction.

The FRET from excited donors to acceptors can be judged by spectral overlap between donor emission and acceptor absorption.[19] Thus, next we prepared pure PBI micelles in aqueous solution according to previously reported procedures,[16] and compared the UV-vis absorption spectrum of PBI micelles as acceptors with the emission spectra of BCz **1–3** donor units in the hydrophobic environment of SDS micelles (Fig. 1 and Fig. S5, ESI†). The emission band of BCz **1** within the confined interior space of SDS micelles does not overlap with the absorption band of pure PBI micelles (Fig. S5, ESI†) suggesting that no FRET can occur between BCz **1** donors and PBI dye acceptors. On the other hand, the broad emission bands from the excited states of stacked BCz **2** or **3**, *i.e.* intramolecular excimers, lead to spectral overlap with the absorption of PBI micelles (Fig. 1b and Fig. S5, ESI†). These results suggest that FRET can occur between BCz **2** or **3** donors and PBI micelle acceptors.

Following the studies with the model micelle, we then explored the functional PBI micelles. Like SDS micelles, the interior of PBI micelles is hydrophobic and thus can load hydrophobic biscarbazoles into their interior. Functional PBI **4** micelles were prepared as follows: biscarbazole **1**, **2** or **3** (5.0 mg of each) was dissolved in THF (1.0 mL) and a portion of 200 μL of the respective THF solution was slowly added into PBI micelle solution (4.0 mL) under stirring, and then ultrasonicated to dissolve biscarbazoles (Fig. 2b). The morphologies of these functional PBI micelles were determined by TEM measurements. These BCz-loaded PBI micelles have an average size of 6–9 nm in diameter (Fig. 2a and Fig. S6, ESI†), which is slightly larger than unloaded PBI **4** dye micelles (4–6 nm)[16] due to BCz encapsulation. The hydrophobic interior could be visualized in a magnified TEM image (Fig. 2a, inset) which displays slight lightness (low electron density) relative to the hydrophilic exterior staining with uranyl acetate (relative darkness). Dynamic light scattering (DLS) analysis showed that the size of these functional micelles is independent of scattering angles further confirming the spherical shape of these morphologies (Fig. 2c).

Compared with pure PBI micelles, these BCz-loaded micelles show an additional fluorescence band at 360–480 nm (Fig. 3c), which arose from the emission of stacked conformation of biscarbazole donors within PBI micelles in aqueous solution.

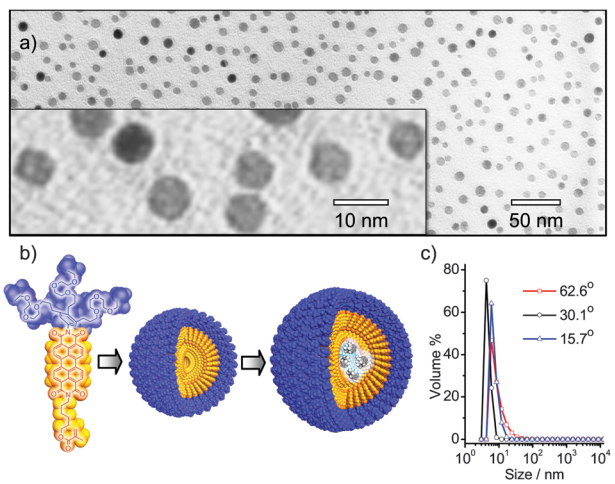


Fig. 2 (a) TEM image of BCz **2**-loaded PBI micelles prepared in aqueous solution, inset: a magnified section; [PBI **4**] = 0.17 mg mL^{-1}. (b) Schematic illustration based on space-filling models for the loading of BCz **2** into PBI micelles. (c) Size distribution of BCz **2**-loaded PBI micelles in aqueous solution determined by DLS at the scattering angles of 15.7°, 30.1° and 62.6°.

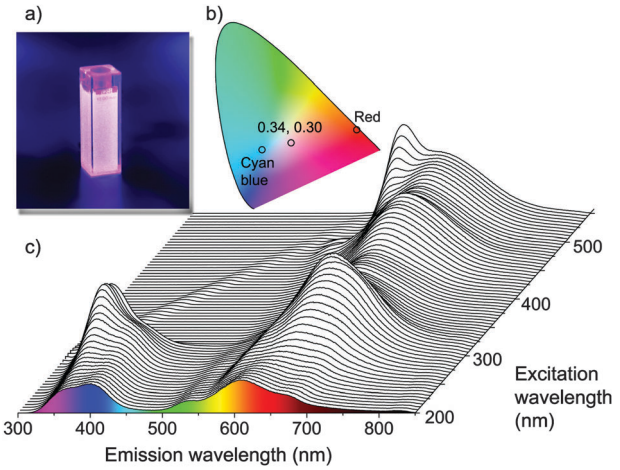


Fig. 3 (a) Photograph of BCz **2**-loaded PBI micelles in aqueous solution under a UV lamp. (b) CIE 1931 chromaticity diagram. The circles indicate the colour coordinates for the cyan blue fluorescence of biscarbazole excimers (0.21, 0.27), the red fluorescence of pure perylene micelles (0.65, 0.35) and white fluorescence coordinates (0.34, 0.30) for the functional micelles. (c) Fluorescence spectra of BCz **2**-loaded PBI dye micelles in aqueous solution at the excitation wavelengths from 200 nm to 550 nm in a 5 nm-step. [PBI **4**] = 0.17 mg mL^{-1}.

Moreover, when the interior biscarbazoles of PBI micelles were excited at the short wavelength of 250–330 nm, the characteristic red broad fluorescence band of PBI dyes[14–16] was observed (Fig. 3c), suggesting that FRET occurred from excited biscarbazoles to PBI dyes within the functional micelles. Most interestingly, white fluorescence was observed with CIE chromaticity coordinates (0.34, 0.30) for BCz-**2** loaded PBI micelles under a UV lamp (Fig. 3a and b). This interesting phenomenon is due to partial energy transfer within functional micelles that leads to the emission of two fluorescence colours, *i.e.* cyan-blue fluorescence (CIE coordinates: 0.21, 0.27) from biscarbazole donors and red fluorescence (CIE coordinates: 0.65, 0.35) from PBI dyes. The two fluorescence colours are complementary (Fig. 3b), and thus their combination leads to white fluorescence. Recently, it has been reported that white light can be achieved by tuning the contributions of three luminescent colours, *i.e.* blue, green, and red,[7,9,12,14] or two luminescent colours, *i.e.* blue and orange.[8] Our present example relates to the second case, since white-light emission is also achieved from two fluorescence colours which are in our case, however, cyan-blue and red (Fig. 3b), and not the previously reported blue and orange combination.

It is interesting to note that common white-light emitting diodes (WLEDs) are based on the same colour "design" principle, *i.e.* a more narrow but quite intense blue emission band combined with a second broad orange-red emission band. The major difference, however, is that in the macroscopic WLED the conversion of blue light from a GaN LED (λ_{max} = 465 nm) is achieved by a conventional absorption process by a Ce^{3+}:YAG phosphor whilst the energy transfer by FRET in our micellar nanosystem is a resonant quantum mechanical process. Also based on size, our micellar nanobulbs are more related to quantum dots than to the macroscopic devices.

To quantify the partial energy transfer and the white light fluorescence phenomenon, we calculated the efficiency of FRET within these functional micelles to be 0.46 and 0.70 for BCz **2**- and BCz **3**-loaded PBI micelles, respectively (for details see ESI†). Because this value is too large for BCz **3**-loaded micelles, white colour could not be realized, pinpointing the challenge in the supramolecular design.

In summary, we have demonstrated FRET within dye micelles by loading biscarbazoles as energy donors into the hydrophobic interior of PBI micelles that act as acceptors. Our white-light emitting, water-soluble BCz **2**-loaded PBI micelles are unique because they represent the smallest imaginable bulb-shaped white-light emitting nano luminary systems accomplished from only two fluorescence colour components, *i.e.* cyan blue and red.

Financial support from the Deutsche Forschungsgemeinschaft DFG (grant project: WU 317/11) is gratefully acknowledged.

Notes and references

1 A. Kaeser and A. P. H. J. Schenning, *Adv. Mater.*, 2010, **22**, 2985; R. Bhosale, S. Bhosale, G. Bollot, V. Gorteau, M. D. Julliard, S. Litvinchuk, J. Mareda, S. Matile, T. Miyatake, F. Mora, A. Perez-Velasco, N. Sakai, A. L. Sisson, H. Tanaka and D. H. Tran, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 1044.
2 J.-H. Ryu, D.-J. Hong and M. Lee, *Chem. Commun.*, 2008, 1043; F. Biedermann, E. Elmalem, I. Ghosh, W. M. Nau and O. A. Scherman, *Angew. Chem., Int. Ed.*, 2012, **51**, 7739.
3 For recent reviews, see: K. T. Kamtekar, A. P. Monkman and M. R. Bryce, *Adv. Mater.*, 2010, **22**, 572; M. C. Gather, A. Köhnen and K. Meerholz, *Adv. Mater.*, 2011, **23**, 233.
4 G. Wyszecki and W. S. Stiles, *Colour Science - Concepts and Methods, Quantitative Data and Formulae*, Wiley-Interscience, New York, 2000.
5 C. Giansante, C. Schafer, G. Raffy and A. Del Guerzo, *J. Phys. Chem. C*, 2012, **116**, 21706.
6 R. J. Abbel, R. van der Weegen, E. W. Meijer and A. P. H. J. Schenning, *Chem. Commun.*, 2009, 1697.
7 R. Wang, J. Peng, F. Qiu, Y. Yang and Z. Xie, *Chem. Commun.*, 2009, 6723.
8 S. Park, J. E. Kwon, S. H. Kim, J. Seo, K. Chung, S. Y. Park, D. J. Jang, B. M. Medina, J. Gierschner and S. Y. Park, *J. Am. Chem. Soc.*, 2009, **131**, 14043.
9 R. Abbel, C. Grenier, M. J. Pouderoijen, J. W. Stouwdam, P. E. L. G. Leclère, R. P. Sijbesma, E. W. Meijer and A. P. H. J. Schenning, *J. Am. Chem. Soc.*, 2009, **131**, 833.
10 S. Brovelli, F. Meinardi, G. Winroth, O. Fenwick, G. Sforazzini, M. J. Frampton, L. Zalewski, J. A. Levitt, F. Marinello, P. Schiavuta, K. Suhling, H. L. Anderson and F. Cacialli, *Adv. Funct. Mater.*, 2010, **20**, 272.
11 S. S. Babu, J. Aimi, H. Ozawa, N. Shirahata, A. Saeki, S. Seki, A. Ajayaghosh, H. Möhwald and T. Nakanishi, *Angew. Chem., Int. Ed.*, 2012, **51**, 3391.
12 C. Vijayakumar, V. K. Praveen and A. Ajayaghosh, *Adv. Mater.*, 2009, **21**, 2059; C. Giansante, G. Raffy, C. Schafer, H. Rahma, M. T. Kao, A. G. L. Olive and A. Del Guerzo, *J. Am. Chem. Soc.*, 2011, **133**, 316.
13 K.-P. Tseng, F.-C. Fang, J.-J. Shyue, K.-T. Wong, G. Raffy, A. Del Guerzo and D. M. Bassani, *Angew. Chem., Int. Ed.*, 2011, **50**, 7032.
14 X. Zhang, S. Rehm, M. M. Safont-Sempere and F. Würthner, *Nat. Chem.*, 2009, **1**, 623.
15 D. Görl, X. Zhang and F. Würthner, *Angew. Chem., Int. Ed.*, 2012, **51**, 6328.
16 X. Zhang, Z. Chen and F. Würthner, *J. Am. Chem. Soc.*, 2007, **129**, 4886.
17 F. C. De Schryver, P. Collart, J. Vandendriessche, R. Goedeweeck, A. Swinnen and M. Van der Auweraer, *Acc. Chem. Res.*, 1987, **20**, 159; J. Vandendriessche, P. Palmans, S. Toppet, N. Boens, F. C. De Schryver and H. Masuhara, *J. Am. Chem. Soc.*, 1984, **106**, 8057; J. Vandendriessche, M. Van der Auweraer and F. C. De Schryver, *Bull. Soc. Chim. Belg.*, 1985, **94**, 991.
18 B. L. Bales, L. Messina, A. Vidal, M. Peric and O. R. Nascimento, *J. Phys. Chem. B*, 1998, **102**, 10347.
19 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum Press, New York, 1999.