Electronic Supporting Information

White-light emitting dye micelles in aqueous solution

Xin Zhang, Daniel Görl and Frank Würthner*

Universität Würzburg, Center for Nanosystems Chemistry & Institut für Organische Chemie
Am Hubland, 97074 Würzburg, Germany
*E-mail: wuerthner@chemie.uni-wuerzburg.de; Fax: +49 (0) 931-31-84756

Table of Contents

1. Materials and methods

2. Synthesis and characterization of biscarbazoles
   Figure S1-S4

3. UV-vis absorption and fluorescence spectroscopy
   Figure S5-S6

4. TEM characterization of functional micelles
   Figure S7

5. Supporting references
1. Materials and methods.

Carbazole, 1, 6-dibromohexane, 1, 3-dibromopropane and sodium dodecyl sulfate (SDS) were purchased from commercial suppliers. The syntheses of biscarbazoles BCz 1, 2 and 3 are described in the next section. Perylene bisimide PBI 4 was synthesized according to our previously reported procedure.[1]

Loading of BCzs in SDS micelles. SDS (1.0 g) was added into water (100 mL) and subsequently ultrasonicated to form micelles. A portion of 100 µL of the THF solution of BCz 1, 2 or 3 (5.0 x 10⁻⁴ M) was slowly added into the SDS micelle solution (10 mL) under stirring, followed by ultrasonication to form a homogenous solution.

Quantification of partial energy transfer. To quantify the partial energy transfer and white light phenomenon, we calculated the efficiency (E) of FRET within BCz-loaded functional PBI micelles by using the equations (1), (2) and (3).[2]

\[
J(\lambda) = \frac{\int F_0(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda}{\int F_0(\lambda) d\lambda} \quad (1)
\]

\[
R_0 = 0.211 \left[ k^2 \eta^4 \Phi_D J(\lambda) \right]^{1/6} \quad (2)
\]

\[
E = \frac{R_0}{R_0 + r_{DA}} \quad (3)
\]

In these equations \( \varepsilon_A \) is extinction coefficient of acceptor absorption, \( k^2 \) is the orientation factor (\( k^2 = 2/3 \) for random orientation of chromophores), \( \eta \) is the refractive index of the medium (\( \eta = 1.333 \)\(^1\), \( \Phi_D \) is the fluorescence quantum yield of donor in the absence of an acceptor (\( \Phi_D = 0.42 \) and 0.38 for BCz 2 and BCz 3 in micelles in aqueous solution, respectively, and \( r_{DA} \) is the donor-to-acceptor average distance (\( r_{DA} = 3.9 \) nm for BCz 2-loaded PBI micelles, \( r_{DA} = 3.1 \) nm for BCz 3-loaded PBI micelles determined from TEM measurements). For the functional micelles, biscarbazoles and PBI 4 serve as energy donors (D) and acceptor (A), respectively. The overlap integral \( J(\lambda) \) between donor emission and acceptor absorption is closely related to the energy transfer efficiency \( E \) according to the equations (2) and (3). Using the equation (1), the spectral overlap integral was calculated to be 3.69 x 10⁻¹⁴ M⁻¹ cm⁻¹ nm⁻⁴ for BCz 2-loaded PBI micelles and 2.88 x 10⁻¹⁴ M⁻¹ cm⁻¹ nm⁻⁴ for BCz 3-loaded PBI micelles. \( R_0 \) is the Förster distance at which the energy transfer efficiency is 50%, which was calculated to be 3.77 nm and 3.56 nm for BCz 2- and BCz 3-loaded PBI micelles, respectively, according to the equation (2). Thus, the energy transfer efficiencies \( E \) can be estimated as 0.46 and 0.70 for BCz 2-loaded and BCz 3-loaded PBI micelles, respectively, from the equation (3).

---

1 Although we do not know the exact refractive index given within our micelles this value for water appears acceptable. For aliphatic solvents such as \( n \)-pentane (\( \eta = 1.358 \)) the values are almost the same whilst they are larger for aromatic solvents such as toluene (\( \eta = 1.497 \)).
Transmission electron microscopy (TEM) measurements were performed on a Siemens Elmiskop 101 electron microscope operating at an acceleration voltage of 80 kV. For the observation of aggregates, a drop of sample suspension was placed on 300-mesh formvar copper grids coated with carbon. About 2 min after the deposition, the grid was tapped with filter paper to remove surface water. Negative staining was performed by addition of a drop of aqueous uranyl acetate solution (0.5 %) onto the copper grid. After 1 min, the surface water on the grid was removed by tapping with filter paper.

Dynamic light scattering (DLS) measurements were performed at room temperature on a N5 Submicron Particle Size Analyzer (Beckman Coulter) using a 25 mW helium-neon laser (632.8 nm). Samples were filtered through 0.45 µm filters to remove dust before measurement. Data were collected and analyzed with PCS control software.

UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 40P spectrophotometer.

Fluorescence spectroscopy. The steady-state fluorescence spectra in solution were recorded under ambient conditions on a PTI QM4-2003 fluorescence spectrometer and corrected against photomultiplier and lamp intensity. The slit width of both monochromators was 5.0 nm.

NMR spectroscopy. ¹H NMR, ¹³C NMR, ¹H, ¹³C-Heteronuclear Single Quantum Correlation (HSQC), ¹H, ¹³C-Heteronuclear Multiple Bond Correlation (HMBC) were recorded at 300 K on a Bruker Avance 400 (400 MHz) spectrometer. ¹H NMR and ¹³C NMR signals were assigned with the aid of two-dimensional ¹H, ¹³C-HSQC and ¹H, ¹³C-HMBC spectra. Multiplicities for proton signals are abbreviated as s, t, and m for singlet, triplet, and multiplet, respectively.

2. Synthesis and characterization of biscarbazoles

BCz 1 was synthesized according to the literature with some modifications. Ethylene glycol (10.0 g, 9 mL, 0.161 mol), pyridine (150 mL) and tosyl chloride (120 g, 0.630 mol) were mixed with vigorous stirring at 0 °C. The reaction mixture was kept in the salt/ice bath with stirring for 8 h. Then, cold water (600 mL) was poured into the reaction mixture and stirred for 15 min. The ditosylate of ethylene glycol was separated by filtration and washed with water and ethanol, and dried under vacuum.

The ditosylate of ethylene glycol (30.0 g, 0.081 mol), carbazole (16.0 g, 0.097 mol), and sodium hydroxide (20 g, 0.50 mol), water (13 mL) and acetone (150 mL) were mixed and stirred for 30 min, then refluxed for 6 h. The resulting mixture was condensed to half of its volume by evaporation. Water (350 mL) was poured into the reaction mixture with stirring to produce brown
precipitate, which was collected by filtration and washed with water for 3 times, then dried in vacuum. The crude product was extracted with CH$_2$Cl$_2$ and purified by silica gel column chromatography (CH$_2$Cl$_2$/hexane = 1/2) to give 9.5 g (0.026 mol, 54%) of the final product as a white solid.

**BCz 1:**

$^1$H NMR (400 MHz, CDCl$_3$, 300 K, TMS) (Fig. S1): $\delta = 4.71$ (s, 4H, 2-CH$_2$), 7.18-7.38 (m, 12H, ArH), 8.05 (d, $J = 3.84$ Hz, 4H, ArH) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$, 300 K, TMS) (Fig. S1): $\delta = 41.2$ (C$_7$, 2-CH$_2$), 107.8 (C$_4$ in carbazole rings), 119.3 (C$_3$ in carbazole rings), 120.5 (C$_1$ in carbazole rings), 123.2 (C$_5$ in carbazole rings), 125.8 (C$_2$ in carbazole rings), 140.1 (C$_6$ in carbazole rings) ppm. MS (ESI) calculated for C$_{26}$H$_{20}$N$_2$: 360.16, found: 360.1 [M$^+$]. IR: $\tilde{\nu}$ (cm$^{-1}$) = 3049, 2948, 2884, 1625, 1593, 1484, 1464, 1450, 1353, 1334, 1232, 1204, 1253, 1195, 1150, 1062, 1014, 1000, 960, 926, 893, 846, 773, 744, 716, 618. Fluorescence ($\lambda_{ex}$ = 300 nm): $\lambda_{em}$ = 348 nm, 364 nm (tetrahydrofuran). Elemental analysis: calcd (%) for C$_{26}$H$_{20}$N$_2$: C 86.60, H 5.92, N 7.52; found: C 86.29, H 5.59, N 7.69. Melting point: 302.5 °C (DSC).

**BCz 2.** Carbazole (10.0 g, 0.06 mmol), 1, 3-dibromopropene (5.0 g, 0.025 mmol) and benzytriethyl ammonium chloride (1 g) and benzene (75 mL) were added into the aqueous solution of 50 % sodium hydroxide (25 mL water, 25 g NaOH). The mixture was refluxed under stirring for 4 h and cooled to room temperature. CH$_2$Cl$_2$ (150 mL) was added into the reaction mixture. The organic phase was separated and washed with water for 3 times and condensed under reduced pressure. The crude product was purified by silica gel column chromatography (CH$_2$Cl$_2$/hexane = 1/3) to give BCz 2 as a white solid.

**BCz 2:**

$^1$H NMR (400 MHz, CDCl$_3$, 300 K, TMS) (Fig. S2): $\delta$ 2.45-2.49 (m, 2H, -CH$_2$), 4.35 (t, $J = 3.68$ Hz, 4H, -NCH$_2$), 7.20-7.27 (m, 12H, ArH), 7.41 (m, 8H, ArH), 8.13 (m, 4H, ArH). $^{13}$C NMR (100 MHz, CDCl$_3$, 300 K, TMS) (Fig. S2): $\delta$ = 27.9 (C$_8$, -CH$_2$), 40.5 (C$_7$, 2-CH$_2$), 108.4 (C$_4$ in carbazole rings), 119.1 (C$_3$ in carbazole rings), 120.5 (C$_1$ in carbazole rings), 123.0 (C$_5$ in carbazole rings), 125.8 (C$_2$ in carbazole rings), 140.1 (C$_6$ in carbazole rings). IR: $\tilde{\nu}$ (cm$^{-1}$) =3416, 3045, 2931, 1625, 1596, 1483, 1463, 1451, 1383, 1326, 1256, 1246, 1219, 1195, 1153, 1120, 1064, 1019, 999, 923, 837, 781, 744, 718, 641, 615. MS (ESI): calculated for C$_{27}$H$_{22}$N$_2$: 374.1783, found: 374.1778 [M$^+$]. UV-vis (MeOH): $\lambda_{abs}$ ($\varepsilon$, M$^{-1}$cm$^{-1}$) = 293 nm (3.27 x 10$^4$), 329 nm (0.74 x 10$^4$), 344 nm (0.81 x 10$^4$). Fluorescence ($\lambda_{ex}$ = 295 nm): $\lambda_{em}$ = 349 nm, 365 nm (tetrahydrofuran). Elemental analysis: calcd (%) for C$_{27}$H$_{22}$N$_2$: C 86.60, H 5.92, N 7.48; found: C 86.11, H 5.83, N 7.52. Melting point: 178.6 °C (DSC).
BCz 3 was synthesized according to the literature \(^5\) with some modifications. Carbazole (10.0 g, 0.06 mmol), 1, 6-dibromohexane (6.0 g, 0.024 mmol) and benzyltriethylammonium chloride (BTEAC, 1.0 g) and benzene (75 mL) were added to an aqueous solution of sodium hydroxide (25 mL water, 25 g NaOH). The mixture was refluxed under stirring for 4 h and cooled to room temperature. CH\(_2\)Cl\(_2\) (150 mL) was added to the reaction mixture. The organic phase was separated and washed with water for 3 times, and condensed under reduced pressure. The crude product was purified by silica gel column chromatography (CH\(_2\)Cl\(_2\)/hexane = 1/3→1/6) to give BCz 3 as a white solid.

**BCz 3:**
\(^1\)H NMR (400 MHz, CDCl\(_3\), 300 K, TMS) (Fig. S3): \( \delta = 1.39 \) (m, 4H, 2-CH\(_2\)CH\(_2\)CH\(_2\)N-), 1.83 (m, 4H, 2-CH\(_2\)CH\(_2\)CH\(_2\)N-), 4.24 (t, \( J = 3.54 \) Hz, 4H, 2-CH\(_2\)CH\(_2\)CH\(_2\)N-), 7.21-7.46 (m, 12H, ArH), 8.10 (m, 4H, ArH). \(^1\)C NMR (100 MHz, CDCl\(_3\), 300 K, TMS) (Fig. S3): \( \delta = 27.0 \) (C\(_9\), 2-CH\(_2\)-), 28.8 (C\(_8\), 2-CH\(_2\)-), 42.8 (C\(_7\), 2-CH\(_2\)-), 108.6 (C\(_4\) in carbazole rings), 118.7 (C\(_3\) in carbazole rings), 120.3 (C\(_1\) in carbazole rings), 122.8 (C\(_5\) in carbazole rings), 125.6 (C\(_2\) in carbazole rings), 140.3 (C\(_6\) in carbazole rings). MS (ESI) calculated for C\(_{30}\)H\(_{28}\)N\(_2\): 416.2252, found: 439.21576 [M+Na]\(^+\). IR: \( \tilde{\nu} \) (cm\(^{-1}\)) = 3051, 2928, 1625, 1593, 1482, 1450, 1379, 1347, 1325, 1244, 1222, 1197, 1149, 1120, 1058, 1021, 997, 964, 922, 844, 815, 773, 748, 720, 632, 615. Fluorescence (\( \lambda_{\text{ex}} = 310 \) nm): \( \lambda_{\text{em}} = 350 \)nm, 367 nm (tetrahydrofuran). Elemental analysis: calcd (%) for C\(_{30}\)H\(_{28}\)N\(_2\): C 86.50, H 6.78, N 6.72; found: C 86.64, H 6.73, N 6.68. Melting point: 123 °C (DSC).

![Fig. S1. \(^1\)H, \(^1\)C-HMQC NMR spectrum of BCz 1 in CDCl\(_3\) with corresponding signal assignments. \(^1\)H NMR and \(^1\)C NMR spectra are also shown in \(^1\)H, \(^1\)C-HSQC NMR spectrum.](image-url)
Fig. S2. $^1$H, $^{13}$C-HSQC NMR spectrum of BCz 2 in CDCl$_3$ with corresponding signal assignments. $^1$H NMR and $^{13}$C NMR spectra are also shown in $^1$H, $^{13}$C-HSQC NMR spectrum.

Fig. S3. $^1$H, $^{13}$C-HSQC NMR spectrum of BCz 3 in CDCl$_3$ with corresponding signal assignments. $^1$H NMR and $^{13}$C NMR spectra are also shown in $^1$H, $^{13}$C-HSQC NMR spectrum.
3. UV-vis absorption and fluorescence spectroscopy

**Fig. S4.** a) Extended and stacked conformations of BCz 2 based on space-filling (CPK) models from semi empirical AM 1 calculation. b) UV-vis absorption spectra of BCz 2 in methanol at different concentrations.

**Fig. S5.** a) Top: Fluorescence spectrum of BCz 1 in THF, $c = 5.0 \times 10^{-6}$ M, bottom: fluorescence spectrum of BCz 1 within sodium dodecyl sulfate (SDS) micelles in aqueous solution, $c = 5.0 \times 10^{-6}$ M. b) Top: Fluorescence spectrum of BCz 3 in THF, $c = 5.0 \times 10^{-6}$ M, bottom: fluorescence spectrum of BCz 3 within SDS micelles in aqueous solution, $c = 5.0 \times 10^{-6}$ M. UV-vis absorption spectra of PBI 4 micelles in aqueous solution are shown in gray in a) and b).
4. TEM characterization of functional micelles

**Figure S6.** TEM image of BCz 3-loaded PBI micelles prepared in aqueous solution.

5. Supporting references