SUPPORTING INFORMATION

Dual Thermo- and Photo-Responsive Micelles Based on Miktoarm Star Polymers

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Experimental details and characterization data for the synthesis of 6-[4-(4’-isobutyloxyphenylazo)pheniloxy]hexyl methacrylate:

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\begin{align*}
\text{4-Isobutyloxynitrobenzene (1).} & \quad \text{2-Methyl-1-propanol (5.33 g, 71.90 mmol), } p- \\
\text{nitrophenol (10.05 g, 71.90 mmol), and diisopropylazidocarboxylate (14.53 g, 71.90 mmol) were dissolved in dry THF (50 mL) under argon atmosphere and while being cooled in an ice-water bath. Subsequently, a solution of triphenylphosphine (18.85 g, 71.90 mmol) in 25 mL of dry THF was added dropwise while stirring. The mixture was stirred at ambient temperature overnight, the solvent was evaporated and the residue dissolved in dichloromethane. The solution was washed twice with a saturated Na}_2\text{CO}_3 \text{ solution, twice with water, and then with brine. The organic phase was dried, concentrated and purified by flash column chromatography on silica gel using hexane/ethyl acetate (8:2) as eluent. Yield: 80\%. IR (KBr),} \nu (\text{cm}^{-1}): 1592, 1519, 1501, 1344, 1268, 1112, 845. \text{^1H-NMR (CDCl}_3, 400MHz) } \delta \text{ (ppm): 8.21-8.18 (m, 2H), 6.96-}
\end{align*}
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6.93 (m, 2H), 3.81 (d, 2H, J=6.5 Hz), 2.10-2.13 (m, 1H), 1.05 (d, 6H, J= 6.7 Hz). $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 164.3, 140.8, 125.9, 114.4, 75.1, 28.1, 19.1.

4-Isobutiloxyaniline (2). Hydrazine monohydrate (98%, 3.5 mL, 71.71 mmol) was added dropwise to a solution of the nitrobenzene derivative (1) (7.00 g, 35.85 mmol) in ethanol (70 mL). After the solution was heated to 40 °C, activated Raney nickel was added and the mixture stirred until no further hydrogen formation was observed. The resulting mixture was filtered to remove the Raney nickel, and the ethanol was removed under reduced pressure. The crude product was dissolved in diethyl ether (60 mL), washed with water and brine, and dried with anhydrous magnesium sulphate. The solvent was distilled off giving the aniline as a yellow oil that was used without further purification. Yield: 90%. IR (KBr),ν (cm$^{-1}$): 3433, 3358, 1592, 1236, 1036, 823. $^1$H-NMR (CDCl$_3$, 400MHz) δ (ppm): 6.75-6.73 (m, 2H), 6.65-6.62 (m, 2H), 3.64 (d, 2H, J=6.5 Hz), 3.40 (s broad, 2H), 2.04-2.10 (m, 1H), 1.00 (d, 6H, J= 6.7 Hz). $^{13}$C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 152.5, 139.8, 116.5, 115.6, 75.2, 28.3, 19.3.

4-Isobutyloxy-4′-hydroxyazobenzene (3). A mixture of aniline (2) (5.21 g, 31.50 mmol) and HCl 6 M (15 mL) was cooled into an ice bath. A 2.5 M NaNO$_2$ solution (20 mL, 31.50 mmol) was added dropwise to the mixture and it was kept stirring in the ice bath. Subsequently, a solution of phenol (2.96 g, 31.50 mmol) in 2 M NaOH (25 mL) was carefully added. The product was precipitated upon addition of HCl until neutral pH and it was purified by flash column chromatography on silica gel using dichloromethane as an eluent. The product was obtained as a yellow powder. Yield: 65%. IR (KBr),ν (cm$^{-1}$): 3137, 1599, 1586, 1503, 1261, 1149, 839. $^1$H-NMR (CDCl$_3$, 400MHz) δ (ppm): 7.87-7.85 (m, 2H), 7.84-7.82 (m, 2H), 7.00-6.98 (m, 2H), 6.94-6.92 (m, 2H), 3.81 (d, 2H, J=6.5 Hz), 2.10-2.13 (m, 1H), 1.05 (d, 6H, J= 6.7 Hz). $^{13}$C-NMR
6-[4-(4'-isobutyloxyphenylazo)phenoxy] hexanol (4). A solution of 4-isobutyloxy-4'-hydroxyazobenzene (3) (3.0 g, 11.1 mmol) and 6-chloro-1-hexanol (1.8 g, 13.3 mmol) in butanone (60 mL) was prepared. 18-Crown-6 (0.05 g) and potassium carbonate (3.1 g, 22.2 mol) were added. The suspension was stirred and heated under reflux for 24 h. Subsequently, it was filtered and concentrated. The crude product was purified by flash column chromatography on silica gel using dichloromethane as eluent. The product was obtained as a yellow powder. Yield: 60%. IR (KBr), υ (cm\(^{-1}\)): 3300, 1601, 1580, 1496, 1465, 1237, 844. \(^1\)H- NMR (CDCl\(_3\), 400MHz) δ (ppm): 7.87-7.85 (m, 4H), 6.94-6.92 (m, 4H), 4.03 (t, 2H, J=6.5 Hz), 3.80 (d, 2H, J=6.6 Hz), 3.65 (c, 2H, J=6.5 Hz), 2.12-2.03 (m, 1H), 1.88-1.75 (m, 2H), 1-1.67-1.56 (m, 2H), 1.37-1.21 (m, 4H), 1.05 (d, 6H, J=6.7 Hz). \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) δ (ppm): 161.3, 146.9, 124.3, 114.7, 114.6, 74.7, 68.1, 62.9, 32.7, 29.2, 28.3, 25.9, 25.6, 19.3.

6-[4-(4'-isobutyloxyphenylazo)phenoxy]hexyl methacrylate (AZO): A solution of 6-[4-(4'-isobutyloxyphenylazo)phenoxy] hexanol (4) (0.8 g, 2.2 mmol) and triethylamine (0.4 mL, 2.6 mmol) in dry THF was prepared. The solution was stirred and acryloyl chloride (0.2 mL, 2.6 mmol) was added dropwise under argon atmosphere. The mixture was stirred and heated under reflux f overnight. Then, it was filtered and concentrated. The crude product was purified by flash column chromatography on silica gel using dichloromethane as eluent. The product was obtained as a yellow powder. Yield: 85%. IR (KBr), υ (cm\(^{-1}\)): 1702, 1637, 1602, 1580, 1500, 1470, 1240, 841. \(^1\)H- NMR (CDCl\(_3\), 400MHz) δ (ppm): 7.88-7.85 (m, 4H), 7.00-6.98 (m, 4H), 6.12-6.08 (m, 1H), 5.58-5.52 (m, 1H), 4.14 (t, J= 6.6 Hz, 2H), 4.04 (t, J= 6.4Hz, 2H),
3.80 (d, J = 6.6 Hz, 2H), 2.11-2.03 (m, 1H), 1.95 (dd, J = 1.5, 1.0 Hz, 3H), 1.90 – 1.78 (m, 2H), 1.80 – 1.67 (m, 2H), 1.37-1.21 (m, 4H), 1.05 (d, J = 6.7 Hz, 6H). $^{13}$C- NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm): 167.5, 161.3, 161.0, 146.9, 146.9, 136.5, 125.2, 124.3, 114.6, 114.6, 74.7, 68.1, 64.6, 29.1, 28.6, 28.3, 25.8, 25.7, 19.3, 18.3.

**General Procedures**

*Preparation of the micelles:* For the preparation of the self-assemblies, a solution of 5 mg mL$^{-1}$ of the amphiphilic BC in THF was prepared and Milli-Q water was gradually added while self-assembly was followed by measuring the turbidity. When a constant turbidity value was reached, the mixture was dialyzed against water to remove the organic solvent using a Spectra/Por® dialysis membrane (MWCO 1000) during 3 days. Water suspensions of the micelles with a concentration around 2 mg mL$^{-1}$ were obtained.

*Determination of the critical aggregation concentration (CMC):* The critical micellar concentration was determined by fluorescence spectroscopy using Nile Red as the probe. For the determination of the CMC, the micelles were loaded with Nile Red as follows. 119 µL of a solution of Nile Red in dichloromethane (5·10$^{-6}$ M) was added into a series of and then the solvent evaporated. Afterwards, a water suspension of micelles of a concentration ranging from 1.0·10$^{-4}$ to 1.0 mg mL$^{-1}$ was added to each flask. The micelles suspensions were prepared by diluting the former 2 mg mL$^{-1}$ micellar suspension. In each flask a final concentration of 1.0·10$^{-6}$ M of Nile Red was reached. These solutions were stirred overnight to reach equilibrium before fluorescence was measured. The emission spectra of Nile Red were registered from
560 to 700 nm while exciting at 550 nm. The relationship between fluorescence intensity at the maximum (606 nm) and logarithm of the polymer concentration is non-linear and the onset point corresponds to the CMC.

Preparation of samples for TEM analysis: 5 µL of a 0.5 mg mL⁻¹ water dispersion of self-assemblies was applied to a TEM grid. Water of the sample was removed by capillarity using filter paper. In the cases of heated and irradiated suspension, the samples were placed in the grid and dehydrated immediately after heating in order to maintain the morphology in the desired situation. Subsequently, the sample was stained with uranyl acetate and the grid was dried overnight under vacuum.

Irradiation experiments: The water dispersions of self-assemblies were irradiated during 10 minutes with compact low-pressure fluorescent lamps Philips PL-S 9W emitting between 350 and 400 nm. After this time, the water suspensions were kept in dark.
Figure S1. $^1$H NMR spectra of PAZO$_{17}$, (PDEAA$_{14}$)$_3$ and the corresponding miktoarm polymer PAZO$_{17}$-(PDEAA$_{14}$)$_3$ (from top to bottom).

Figure S2. a) SEC traces of PAZO$_{17}$ (black line), (PDEAA$_{14}$)$_3$ (grey line) and PAZO$_{17}$-(PDEAA$_{14}$)$_3$ (dashed line). b) SEC traces of PAZO$_{17}$ (black line), (PDEAA$_{22}$)$_3$ (grey line) and PAZO$_{17}$-(PDEAA$_{22}$)$_3$ (dashed line). c) SEC traces of PAZO$_{17}$ (black line), (PDEAA$_{55}$)$_3$ (grey line) and PAZO$_{17}$-(PDEAA$_{55}$)$_3$ (dashed line).
Figure S3. a) DSC curves of PAZO\textsubscript{17} (black line), PDEAA\textsubscript{14} (grey line) and PAZO\textsubscript{17}-(PDEAA\textsubscript{14})\textsubscript{3} (dashed line). b) DSC curves of PAZO\textsubscript{17} (black line), PDEAA\textsubscript{22} (grey line) and PAZO\textsubscript{17}-(PDEAA\textsubscript{22})\textsubscript{3} (dashed line). c) DSC curves of PAZO\textsubscript{17} (black line), PDEAA\textsubscript{55} (grey line) and PAZO\textsubscript{17}-(PDEAA\textsubscript{55})\textsubscript{3} (dashed line).
Figure S4. Volume distribution of a water suspension micelles of PAZO$_{17}$-(PDEA$_{55}$)$_3$ at different conditions. Measurement at 40 °C was not possible due to instability of the suspension.
Figure S5. UV-vis spectrum of PAZO$_{17}$-(PDEAA$_{55}$)$_3$ in chloroform (at a concentration of 10$^{-5}$ M) at 20ºC.
**Figure S6.** Emission spectra of the Nile Red (10⁻⁶M in dichloromethane) at different irradiation times (350- 400 nm, 9W)