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Selective and Sensitive Chromo- and Fluorogenic Dual Detection of Anionic Surfactants in Water Based on a Pair of "On–Off–On" Fluorescent Sensors

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Anionic surfactants are widely applied in industrial and domestic detergents, and the detergent wastes are a major component of organic pollutants.[1] As a result of the extensive use of these products, it is very important to detect anionic surfactants in the environment and in water samples. Many well-known techniques in surfactant analysis, including methylene blue method, ion-selective electrodes, capillary electrophoresis method, and so forth, show some limitations in their applicability, such as tedious procedures, large amount of toxic solvents, irreproducibility, and signal instability.[2] Therefore, it is especially attractive to develop new methods for anion-surfactant recognition in water.[3]

Spectrophotometric and spectrofluorometric methods, with their many inherent merits including high sensitivity, high specificity, and real-time in situ response, have been extensively used in scientific research, industrial production, environment or physiological phenomena, and daily life.[4] Martínez-Máñez and co-workers used a hybrid system for colorimetric detection of the anionic surfactant SDS (sodium dodecyl sulfate) with 1 ppm detection limit; Xu and co-workers detected SDS by fluorescence quenching in the presence of Triton X-100 (Triton X-100: isooctylphenolic polyglycol ether); Taguchi and co-workers reported that a detection limit of 2 ppb SDS could be achieved after its enrichment.[5] Inspired by these reports, we provide a pair of relatively sensitive sensors for anionic-surfactant detection due to the formation of 1:1 complex without complicated sample pretreatment. Both sensors showed chromo- and fluorogenic dual responses towards the anionic surfactants.

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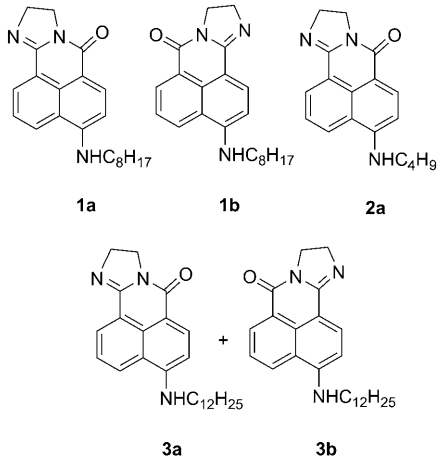
Herein, five related dyes (**1a**, **1b**, **2a**, **3a**, and **3 b**) bearing dihydrogen imidazo[2,1-α]benz[*d*,*e*]isoquinolin-7-one fluorophore were specifically designed and simply synthesized to



detect the anionic surfactant SDS at a relatively low concentration with both absorbance and fluorescence intensity changes. In this array, the *n*-alkyl amino substituents at the 4-position endow these dyes with a comparatively strong hydrophobic interaction with SDS. More stable complexes of dye–SDS may be formed in this situation. Accordingly, the photophysical properties of these dyes will be changed significantly with the addition of SDS. Anionic surfactants can be discriminated from other detected surfactants and ions by this array. The detection limit of SDS was 3.0×10^{-8} M (8.6 ppb) with probe **1b** (or **1a**).

The addition of SDS to a solution of **1b** in neutral water (pH 6.50) resulted in fluorescence quenching of **1b** centered at 526 nm (Figure 1 top) and a regular decrease in absorption spectrum (Figure S2a in the Supporting Information). At SDS concentration ~3.6 mM, the fluorescence was mostly quenched (91%) along with 68% hypochromicity in the absorbance. The Job's plot suggested a 1:1 stoichiometry for

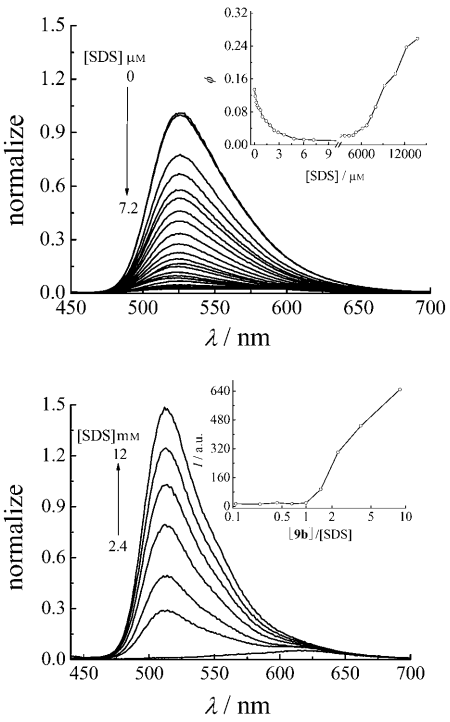


Figure 1. SDS effects on the emission spectra of **1b** aqueous solution. Inset show the changes in fluorescence quantum yield (inset top) and the Job's plot (inset bottom) ([**1b**] = 5.0 mM).

the complex **1b**·SDS (inset in Figure 1 bottom). The association constant (K_s) was determined to be $1.28\times10^6\,M^{-1}$ by fluorescence ($1.62\times10^6\,M^{-1}$ by UV/Vis) from the SDS titration curve (Figure S3 in the Supporting Information), and the dynamic detection window of SDS was 3.0×10^{-8} to 3.6×10^{-6} M. Both the emission and absorption spectra had no evident change in SDS concentration range of 7.2–2400 mM; beyond this the fluorescence and absorbance were recovered and finally exceeded their initial values (Figure 1 bottom and Figure S2b). So, **1b** is an "on–off–on" fluorescent sensor for anionic surfactant SDS.

Similar results were obtained with the addition of SDS to **1a** solution (Figure S4 in the Supporting Information); however, significant red shifts were observed in both the emission and absorption maxima when the concentration of SDS is more than 0.98 mM and was accompanied by a color change from yellow to red. The experimental results indicated the formation of 1:1 complex of **1a**·SDS with an association constant of $1.15\times10^6\,M^{-1}$. The almost same K_s values of **1a**·SDS and **1b**·SDS reveal that the interaction modes of **1a** and **1b** with SDS are alike. Anionic surfactant SDBS (sodium dodecylbenzenesulfonate) shows the similar effects on the spectral properties of **1a** and **1b** (Figure S5 in the Supporting Information).

The pK_a values of **1a** and **1b** are 6.08 and 7.02, respectively. In neutral and acidic solution, both **1a** and **1b** are protonated to some extent. The first decrease in fluorescence intensity and absorbance of **1b** in the presence of small amount of SDS is resulted from the complex formation between **1b** and SDS, which is driven by electrostatic and hydrophobic interactions. The photoinduced electron transfer from the negatively charged head group of SDS to the fluorophore might occur and thus quench the fluorescence of the dye. When the SDS concentration is greater than 2.4 mM, the **1b**·SDS complexes dissociate gradually to rearrange to form SDS micelles with all the dye molecules incorporated into micelle in monomeric form. The lower polarity inside SDS micelle leads to the enhancement of fluorescence intensity and a blue shift in emission wavelength of **1b** (from 526 to 512 nm).[6]

To investigate the effects of alkyl chain length on the formation of dye–SDS complex, we have also studied the effects of SDS on the photophysical properties of **2a**, **3a**, and **3b** (Figures S6–8 in the Supporting Information). The changes in absorption spectra of **2a** and **3a** were similar to that of **1a**, but the variation rates of the former were much slower (Figure 2). The addition of SDS made the fluorescence intensity of **2a** decrease sharply first and then increase slightly, while that of **3a** increased steadily. In the case of **3b**, the addition of SDS resulted in a tiny enhancement in absorbance; whereas the fluorescence intensity decreased at SDS concentrations of less than 30 mM (the fluorescence quenching ratio is 46% at SDS concentrations of ~9.2 mM, that of **1b** is 91% at SDS concentrations of ≈3.6 mM), beyond this, it increased regularly (Figure 2 bottom). Furthermore, Figure 2 illustrates that the dynamic detection

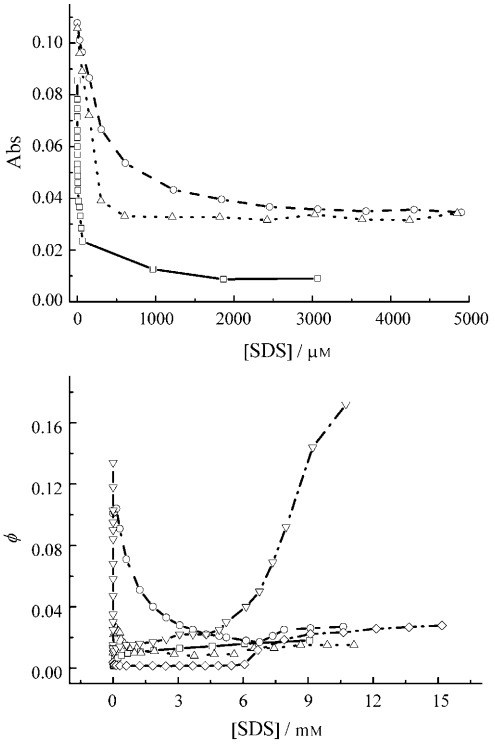


Figure 2. SDS titration curves of **1a**, **1b**, **2a**, **3a** and **3b** in water. Top: □ **1a**; ○ **2a**; △ **3a**. Bottom: □ **3b**; ○ **2a**; △ **1a**; ▽ **1b**; ◇ **3a**.

window of SDS varies with the alkyl chain length, viz., 30 mM–3 mM, 7 mM–0.4 mM and 0.03–3.6 mM with **2a, 3a** and **1a** as probe, respectively. The detection range of SDS is expected to be enlarged when **2a**, **3a** and **1a** are used in parallel.[7]

We have also studied the response of dyes similar to compounds **1a** and **1b**, but with substituents at the 4-positions being *N*,*N*-dimethyl amino (**4a**/**4b**) and *N*-2-hydroxyethyl amino (**5a**/**5b**) groups. The experimental results showed that a small amount of SDS ([SDS] < 100 μM) had no evident effect on the absorption and emission spectra of these compounds, but the existence of large amount of SDS (less than its critical micelle concentration (cmc)) quenched their fluorescence (Figure 3). This indicated that **4** and **5** cannot form

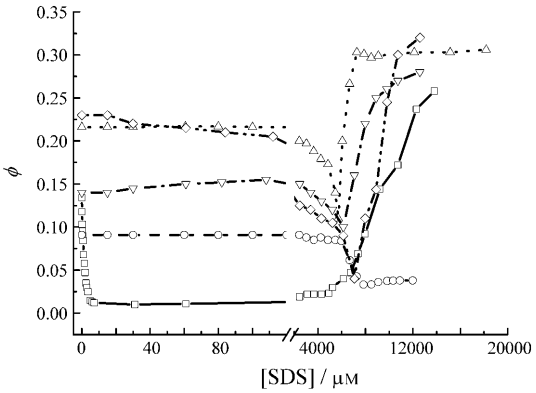


Figure 3. SDS titration curves of **1b**, **4a**, **4b**, **5a**, and **5b** in water. □ **1b**; ○ **5a**; △ **5b**; ▽ **4a**; ◇ **4b**.

1:1 complexes with SDS due to the lacking alkylic chain, but they could form mixed aggregates with SDS at relatively high SDS concentrations (~1 mM) by coulomb interaction.

The above results may indicate that the interaction between **2a** (or **3a**/**3b**/other dyes) and SDS is relatively weak; however, there exists very strong interaction between **1b** (or **1a**) and SDS. The fluorophores of all these compounds are same, but the alkyl chain lengths are different. So, the hydrophobic interaction plays important role in the detection of anionic surfactants. It is of note that **3a** and **3b** have a longer alkylic chain, but they display a worse response than the corresponding compounds **1a** and **1b**, which may be caused by the relatively lower solubility of **3a** and **3b** in water.

Remarkably, the effects of neutral (Triton X-100, Figures S9 and S10 in the Supporting Information) and cationic surfactants (cetyl trimethyl ammonium bromide (CTAB), Figures S11 and S12 in the Supporting Information) on the emission and absorption spectra of **1a** and **1b** are different from that of SDS. In the case of **1a**, CTAB and Triton X-100 did not induce notable wavelength shift. The absorption spectrum had minor change and the fluorescence intensity increased steadily upon addition of CTAB and Triton X-100. As for **1b**, Triton X-100 decreased the fluorescence intensity and absorbance to some extent, while CTAB enhanced them slightly when its concentrations are less than 500 mM (Figure 4). The above results show that charge characters of surfactants are also important in surfactant determination.

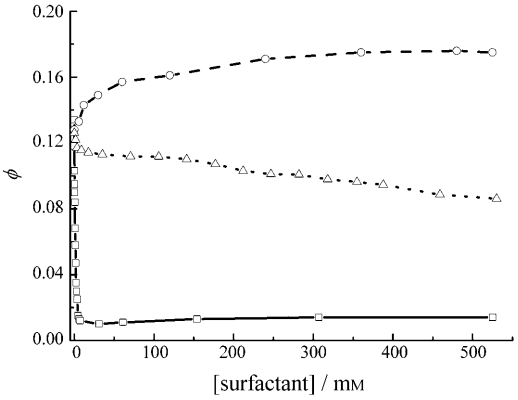


Figure 4. Surfactant titration curves of **1b**. □ SDS; ○ CTAB; △ Triton X-100.

No evident interference was found in the presence of sulfate, nitrate, and halogen at concentrations less than 1 mM.

In buffer solutions with different pH values (pH 0.86, 2.55, 4.84, and 7.05), **1b** showed similar response towards SDS. The ionic strength affected the dye–SDS interaction to some extent. The quenching effect of SDS decreases with increasing ionic strength: in neutral water, and 0.01 M and 0.15 M phosphate buffer solution (pH 7.05), the fluorescence quenching yields are 91, 89 and 65%, respectively, with the addition of one equivalent of SDS. However, the fluorescence intensity of **1b** has minor change upon addition of 20 equivalents of some inorganic anions as well as the nonionic surfactant Triton X-100 and cationic surfactant CTAB (Figure 5) in all three cases.

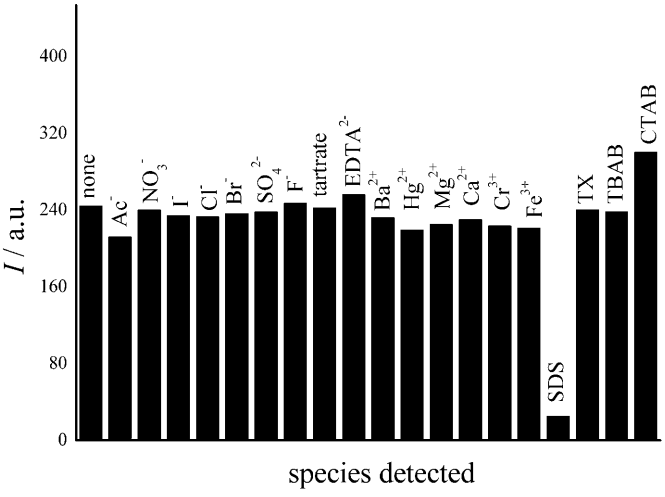


Figure 5. Fluorescence intensities of **1b** (5 μM) in phosphate buffer solution (0.01 M, pH 4.84) in the presence of different species ([SDS] = 5 μM, the concentrations of others are 100 μM).

Figure 6 shows the effects of some anions, cations, CTAB, and Triton X-100 on the detection of SDS. Except for CTAB, no remarkable interference to SDS determination was found in the presence of these chemical species. The existence of 100 μM of cationic surfactant CTAB recovered the fluorescence of **1b**, which might be due to the formation of SDS–CTAB complex, setting **1b** free from the complex **1b**·SDS and resulting in the enhanced fluorescence. However, the addition of terabutylammonium bromine (TBAB, 100 μM) caused negligible change in fluorescence intensity, indicating the weaker interaction between SDS and TBAB because of the shorter alkylic chain length of the latter. The above results proved that the hydrophobic interaction between SDS and dyes played important role in SDS detection.

Table 1. Fingerprints for different species.[a]

Dyes	Array	SDS			CTAB[c]	TX-100[d]	Acidic	Basic
		< 0.2 mM [b]	0.2–6 mM	> 6 mM	> 0.5 mM	> 0.2 mM	solution	solution
1a	UV-435	+	–	–	+	+	–	+
1a	UV-500	–	–	+	–	–	+	–
1a	FL-525	+	–	–	+	+	–	+
1a	FL-600	–	–	+	–	–	+	–
1b	UV-475	+	–	+	–	–	+	–
1b	FL-526	+	–	+	–	–	+	–
3a	FL	–	–	+	+	+	–	–
3b	UV-470	+	+	+	+	+	+	–
3b	FL-525	–	–	+	+	+	+	–

[a] UV-430 and FL-525 represent the UV-vis absorption at 430 nm and emission at 525 nm, respectively; "+" and "–" indicate the outputs are high and low, respectively. [b] When SDS concentrations are less than 5 mM, its concentration can be detected with **1a** or **1b**, and the outputs are varied with SDS concentrations. [c] When CTAB concentrations are less than 0.5 mM, no evident effects on the spectral properties of these dyes were observed. [d] When Triton X-100 concentrations are less than 0.2 mM, no evident effects on the spectral properties of these dyes were observed.

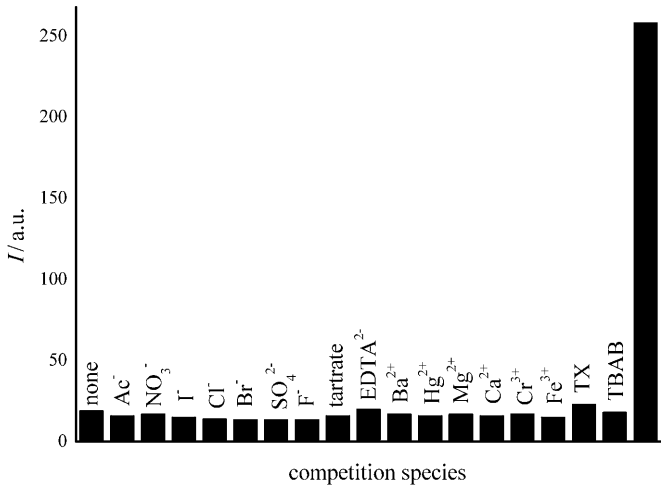


Figure 6. Fluorescence intensities of **1b** (5 μM) in phosphate buffer solution (0.01 M, pH 4.84) containing 10 μM SDS in the presence of different species (the concentrations of all anions are 1 mM, those of cations are 0.1 mM).

Dyes **1a** and **1b** are also sensitive to the pH of the solution (Figures S13 and S14 in the Supporting Information). Protons affect the spectra of **1a** in the way similar to that of SDS, namely, **1a** shows "on-off-on" response towards H^+. The hydroxyl anion makes the absorbance and fluorescence intensity of **1b** decrease, which is similar to the presence of small amount of SDS. So, H^+, OH^-, and other ions (e.g. phosphate, carbonate, etc.) that induce pH variation will disturb the detection of anionic surfactants. Fortunately, anionic surfactants can be differentiated from those ions by combining **1a** with **1b** as shown in Table 1. In addition, different concentration ranges of anionic surfactants can also be distinguished by using the sensor array.

The response of **1a**, **1b**, **3a** and **3b** towards differently charged surfactants and the pH of the solution is shown in Table 1; these data indicate a unique fingerprint for each species. Table 1 reveals that this sensor array can be used to sense anionic surfactants as well as their concentration ranges.

In summary, "on–off–on" fluorescent sensors **1a** and **1b** can be used to chromo- and fluorogenically detect a class of environmentally important anions with high sensitivity and selectivity. Both electrostatic and hydrophobic interactions play important roles in surfactant determination. The dynamic detection range can be adjusted by altering the chain length of substituting group, and it can be enlarged by using analogues in parallel. We have also developed a sensor array for the discrimination of anionic surfactants with different concentration ranges. We believe that the results demonstrated here may provide a strategy for the design of new sensors for chromo- and/or fluorogenic sensing of surfactants in water.

Experimental Section

Reagents: All the solvents and reagents were of analytic grade and used as received. Water used was twice distilled.

Synthesis: The synthesis of **1a**, **1b**, **2a**, **3a**, and **3b**, from commercially available compounds was performed as follows.

***N*-(Aminoethyl)-4-bromonaphthalene-1,8-dicarboximide (6)**: Ethylenediamine (2.0 g, 33.3 mmol) was added to a suspension of 4-bromonaphthalene-1,8-dicarboximide (5.54 g, 20 mmol) in ethanol (50 mL). The mixture was then refluxed for 4 h, after which the solvent was evaporated under vacuum. The product crystallized from ethanol. Yield 85%; m.p. 154.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.65$ (dd, J(H,H) = 8.2, 7.8 Hz, 1H; 7-ArH), 8.56 (dd, J(H,H) = 8.4, 8.2 Hz, 1H; 2-ArH), 8.41 (d, J(H,H) = 7.9 Hz; 1H, 5-ArH), 8.02 (d, J(H,H) = 7.8 Hz, 1H; 5-ArH), 7.82 (dd, J(H,H) = 7.9, 7.6 Hz, 2H; 3,6-ArH), 4.27 (t, J(H,H) = 6.6 Hz, 2H; -N$CH_2$$CH_2NH_2$), 3.07 ppm (t, J(H,H) = 6.6 Hz, 2H; -$NCH_2CH_2NH_2$); MS (70 eV): m/z (%): 318 (1) $[M]^+$.

Synthesis of 2a: Compound **6** (0.2 g , 6.3 mmol) and excess *n*-butyl amine (1 mL) were added to ethylene glycol monomethyl ether (5 mL). The mixture was heated to reflux for 5 h under an N_2 atmosphere and then the solvent was evaporated under vacuum. The product was purified by chromatography by using methanol/dichloromethane (1: 30, v/v) as eluant to give **2a** (110 mg, yield 50%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J(H,H) = 7.3 Hz, 1H), 8.30 (d, J(H,H) = 7.2 Hz, 1H), 7.92 (d, J(H,H) = 7.5 Hz, 1H), 7.50 (t, J(H,H) = 7.8 Hz, 1H), 6.60 (d, J(H,H) = 7.9 Hz, 1H), 4.16 (q, J(H,H) = 6.3 Hz, 4H), 3.36 (t, J(H,H) = 6.3 Hz, 2H), 1.87 (m, J(H,H) = 6.1 Hz, 2H), 1.53 (m, J(H,H) = 6.1 Hz, 2H), 1.00 ppm (t, J(H,H) = 6.1 Hz, 3H); HR-MS (ES+): m/z calcd for $[M+H]^+$: 294.1606; found: 294.1594.

Snythesis of 3a and 3b: Compound **6** (0.2 g, 6.3 mmol) and excess n-dodecyl amine (0.3 g) were added to ethylene glycol monomethyl ether (5 mL). The mixture was heated to reflux for 5 h under an N_2 atmosphere and then the solvent was evaporated under vacuum. The product was purified by chromatography using methanol/dichloromethane (1: 100, v/v) as eluant to give **3a** (80 mg, yield 35%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, J(H,H) = 7.6 Hz, 1H), 8.35 (d, J(H,H) = 8.0 Hz, 1H), 8.00 (d, J(H,H) = 8.4 Hz, 1H), 7.57 (t, J(H,H) = 8.0 Hz, 1H), 6.98 (d, J(H,H) = 8.4 Hz, 1H), 4.18 (m, 4H), 3.38 (t, J(H,H) = 7.2 Hz, 2H) , 1.83 (m, 2H), 1.51 (m, 2H), 1.27 (m, 16H), 0.90 ppm (t, J(H,H) = 6.5 Hz, 3H); ^{13}C NMR (100 MHz): δ = 161.1, 156.2, 148.6, 131.9, 130.7, 127.5, 124.8, 124.4, 121.1, 111.8, 103.9, 53.4, 53.1, 43.9, 43.8, 31.9, 29.7, 29.64, 29.58, 29.47, 29.34, 29.14, 29.05, 27.21, 22.68, 14.12 ppm; HR-MS (ES+): m/z calcd for $[M+H]^+$: 406.2858; found: 406.2854. Compound **3b** was obtained as orange red solid (103 mg, yield 45%). ^{1}H NMR ($CDCl_3$/CD_3OD): δ = 8.34 (d, J(H,H) = 7.2 Hz, 2H), 8.18 (d, J(H,H) = 8.4 Hz, 1H), 7.54 (t, J(H,H) = 8.0 Hz, 1H), 6.67 (d, J(H,H) = 8.8 Hz, 1H), 4.11 (s, 4H), 3.36 (m, 2H), 1.76 (m, 2H) , 1.47 (m, 2H), 1.34 (m, 16H), 0.86 ppm (t, J(H,H) = 6.5 Hz, 3H); ^{13}C NMR (100 MHz): δ = 161.6, 156.1, 150.2, 131.0, 130.7, 129.3, 127.6, 124.3, 123.1, 121.1, 104.3, 104.2, 50.9, 43.6, 43.5, 31.8, 29.5, 29.4, 29.3, 29.2, 28.4, 27.1, 22.5, 13.6 ppm; HR-MS (ES+): m/z calcd for $[M+H]^+$: 406.2858; found: 406.2841.

Synthesis of compounds 1a and **1b**: Compound **6** (0.2 g, 6.3 mmol) and excess *n*-octyl amine (1 mL) were added to ethylene glycol monomethyl ether (5 mL). The mixture was heated to reflux for 5 h under an N_2 atmosphere and then the solvent was evaporated under vacuum. The product was purified by chromatography using methanol/dichloromethane (1: 30, v/v) as eluant to give **1a** (125 mg, yield 60%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J(H,H) = 7.2 Hz, 1H), 8.33 (d, J(H,H) = 8.0 Hz, 1H), 7.96 (d, J(H,H) = 8.0 Hz, 1H), 7.54 (t, J(H,H) = 8.0 Hz, 1H), 6.66 (d, J(H,H) = 8.4 Hz, 1H), 4.16 (m, 4H), 3.36 (m, J(H,H) = 7.2 Hz, 2H), 1.81 (m, 2H), 1.49 (m, 2H), 1.37 (m, 8H), 0.89 ppm (t, J(H,H) = 7.2 Hz, 3H); ^{13}C NMR (100 MHz): δ = 161.2, 155.8, 148.3, 131.5, 130.7, 126.9, 124.7, 123.9, 121.5, 121.1, 112.1, 103.7, 53.8, 43.9, 43.8, 31.8, 29.4, 29.2, 29.1, 27.2, 22.6, 14.1 ppm; HR-MS (ES+): m/z calcd for $[M+H]^+$: 350.2232; found: 350.2219. Compound **1b** was obtained as orange red solid (31 mg, yield 15%). ^{1}H NMR ($CDCl_3$/CD_3OD): δ = 8.44 (dd, J(H,H) = 8.8, 7.6 Hz, 2H), 8.25 (d, J(H,H) = 8.4 Hz, 1H), 7.60 (t, J(H,H) = 8.0 Hz, 1H), 6.75 (d, J(H,H) = 8.8 Hz, 1H), 4.20 (t, J(H,H) = 4.4 Hz, 2H), 4.14 (t, J(H,H) = 4.8 Hz, 2H), 3.65 (s, 1H), 3.43 (t, J(H,H) = 7.2 Hz , 2H) , 1.79 (m, 2H), 1.47 (m, 2H), 1.32 (m, 16H), 0.89 ppm (t, J(H,H) = 3.6 Hz, 3H); ^{13}C NMR (100 MHz): δ = 161.4, 156.6, 151.5, 132.2, 130.9, 130.1, 128.2, 124.6, 122.8, 121.1, 104.6, 43.66, 43.5, 31.8, 29.5, 29.2, 29.1, 28.3, 27.0, 22.4, 13.5 ppm; HR-MS (ES+): m/z calcd for $[M+H]^+$: 350.2232; found: 350.2213.

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