



## Epoxy-based polymer bearing 1-naphthylamine units: highly selective fluorescent chemosensor for ferric ion

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### ABSTRACT

A simple epoxy-based polymer **1** bearing 1-naphthylamine units has been synthesized and its recognition behaviors toward various metal ions have been investigated in THF–water (8:2, v/v) solution. The designed polymer **1** was found to exhibit selective ON–OFF-type fluorosensing behavior toward  $\text{Fe}^{3+}$  ions over other representative metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Hg}^{2+}$  ions.

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Design and development of metal-ion selective fluorescent chemosensors is an increasingly topical field with potential application in industrial, environmental, and biomedical monitoring.<sup>1–3</sup> In particular, the studies of new chemosensors toward  $\text{Fe}^{3+}$  ions among the essential metal ions are quite intriguing because of their importance in many biological and environmental processes. Accordingly, many small molecular systems are being developed to selectively recognize such metal ions.<sup>4–6</sup> Recently, much interest has been focused on polymeric chemosensor bearing metal ion complexing units.<sup>7</sup> In this context, epoxy-based polymers are more interesting because of their attractive properties such as low manufacturing cost, easy processibility, good chemical resistance and dimensional stability, and potential for reuse. In addition, the reactive epoxy groups can be reacted easily with a variety of functional groups such as  $-\text{COOH}$  and  $-\text{NH}_2$ . Furthermore, 1-naphthylamine molecule is currently used in the design of fluorescent sensors owing to its simplicity and sensitivity.<sup>8</sup> Accordingly, the design and synthesis of ferric ion-sensing fluorescent polymeric chemosensors, based on covalently immobilized 1-naphthylamine signaling units, has become a very active area of research. In relation to this, we report herein a simple development of epoxy-based polymer **1** appended with 1-naphthylamine signaling units for the selective recognition of ferric ion over other metal ions examined. To the best of our knowledge, epoxy-based macromolecular probe that selectively shows  $\text{Fe}^{3+}$ -selective fluorescence characteristics has not been reported yet. Our design is particularly interesting because on covalent immobilization of the 1-naphthylamine moiety in the

polymer matrix, migration or leaching of fluorophore molecule can be avoided.

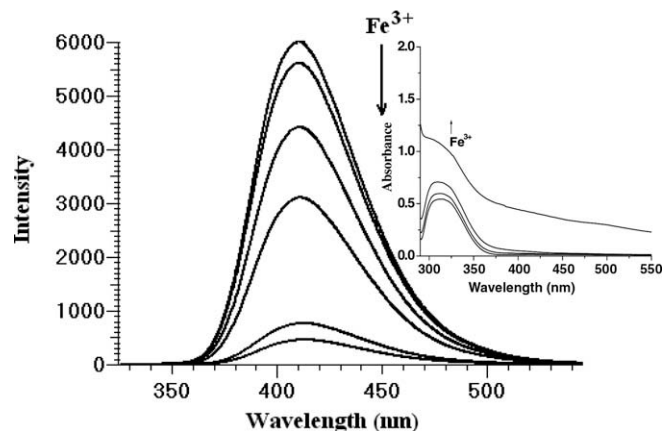
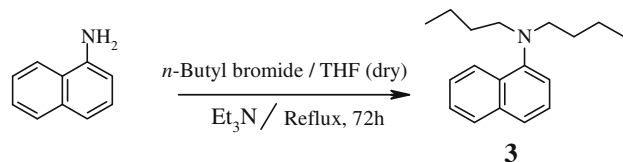
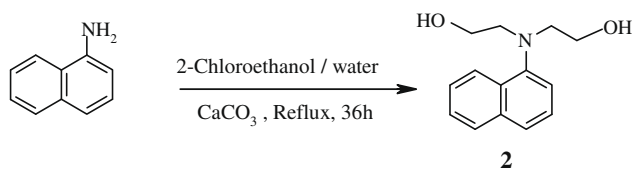
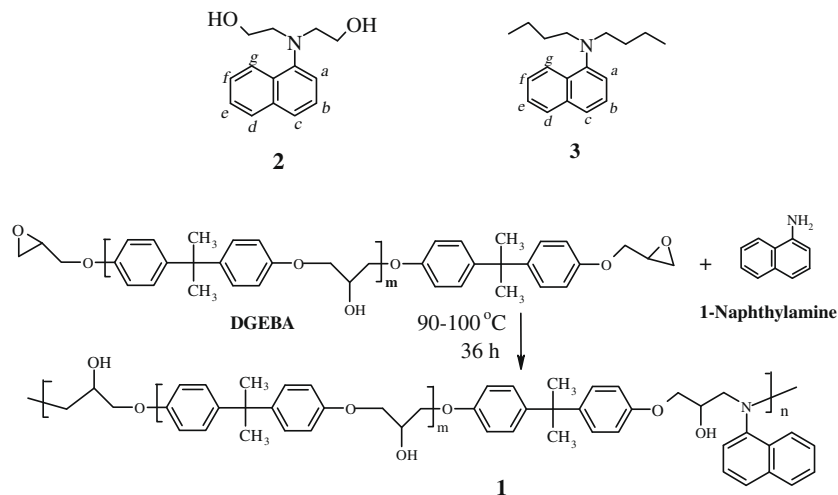
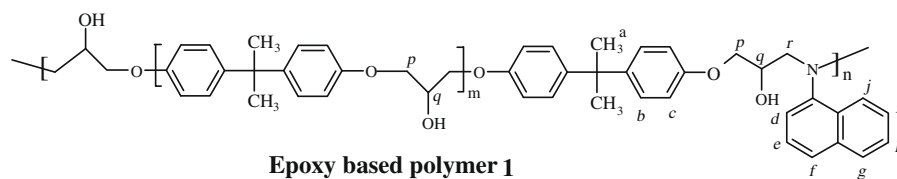
1-Naphthylamine-tethered epoxy-based polymer **1** was prepared<sup>9</sup> as described in the following Scheme 1 by the simple condensation of diglycidyl ether of bisphenol-A (DGEBA) and 1-naphthylamine. Solubility experiments showed that the polymer is soluble in common organic solvents such as THF, 1,4-dioxane,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , DMF, and DMSO. Titled polymer **1** was unequivocally characterized<sup>9</sup> by FT-IR, UV–vis, NMR, GPC, and elemental analyses. The peaks due to the aromatic protons were observed between 8.42 and 6.68 ppm in the  $^1\text{H}$  NMR spectrum.

At the same time, its structurally simplified small molecular analogues **2** and **3** were synthesized<sup>10,11</sup> as model compounds in moderate yield following the methods outlined in Schemes 2 and 3. All these compounds were isolated as pure compounds as evidenced by FT-IR,  $^1\text{H}$  NMR, and elemental analysis.<sup>10,11</sup>

The UV–vis spectrum of **1** in THF–water (8:2, v/v) solution ( $[\mathbf{1}] = 4.99 \times 10^{-2}$  mg/ml;  $\sim 1.49 \times 10^{-4}$  (M) with respect to repeat unit) exhibits the typical 1-naphthylamine absorption band at  $\lambda_{\text{max}} = 315$  nm (inset of Fig. 1). Titration experiments were carried out by using the set of representative metal ions such as  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  (all as sulfates), and  $\text{Hg}^{2+}$  (as chloride) to evaluate the metal ion-binding property of **1**. These studies resulted in cation-induced hyperchromic shift of absorption band for all metal ions. The addition of  $\text{Fe}^{3+}$  produced more pronounced hyperchromic shift clearly indicating the strong binding nature of **1** toward  $\text{Fe}^{3+}$  in its ground state. The UV–vis spectral appearance observed using the model compounds suggests that the involvement of two proximal  $-\text{OH}$  groups for metal ion binding is remarkable in the ground state. Polymer **1** showed strong fluorescence centered

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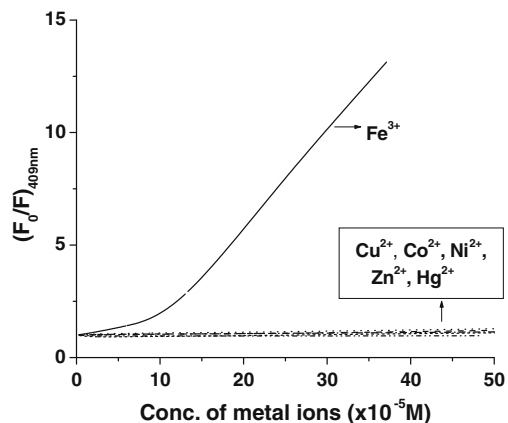


**Figure 1.** Fluorescence spectral changes of **1** ( $4.99 \times 10^{-2}$  mg/ml) with different concentrations of  $\text{Fe}^{3+}$  ion (up to  $37.15 \times 10^{-5}$  M) in THF–water (8:2, v/v) ( $\lambda_{\text{exc}} = 315$  nm); inset: UV–vis spectral change.

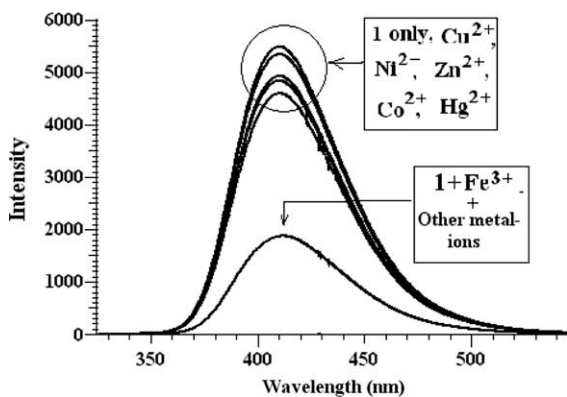
around 409 nm in THF–water (8:2, v/v) ( $[\mathbf{1}] = 4.99 \times 10^{-2}$  mg/ml;  $\sim 1.49 \times 10^{-4}$  M) with respect to repeat unit) at 25 °C. To examine the selectivity of **1** as fluorosensor, responses to diverse metal ions [ $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  (all as sulfates), and  $\text{Hg}^{2+}$  (as chloride)] are compared ( $\lambda_{\text{exc}} = 315$  nm). The fluorescence titration study of **1** with  $\text{Fe}^{3+}$  ion exhibited a drastic decrease in fluorescence intensity (ON–OFF) at 409 nm. **Figure 1** shows the change in emission of **1** upon gradual addition of  $\text{Fe}^{3+}$  ion.

Other representative metal ions, except for the marginally responding  $\text{Cu}^{2+}$  ions, exhibited almost insignificant responses under the same excitation condition. The ability of the metal ions to quench the fluorescence emission of **1** has been estimated by the Stern–Volmer plot (**Fig. 2**). The plot shows more pronounced quenching with  $\text{Fe}^{3+}$  ion over other metal ions studied demonstrating a better chemosensitivity of **1** for  $\text{Fe}^{3+}$  ions.

Further experiments for  $\text{Fe}^{3+}$ -selective sensing were also carried out by adding  $\text{Fe}^{3+}$  to the solution of **1** in the presence of other interfering metal ions (**Fig. 3**). Even in the presence of these com-



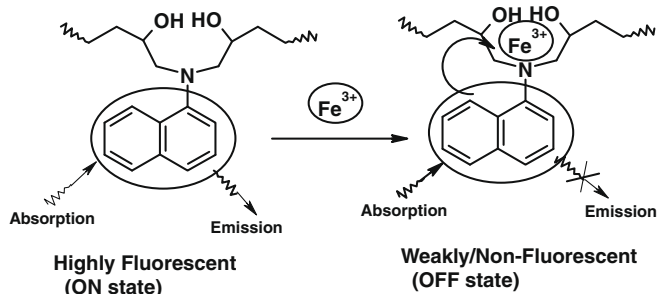
**Figure 2.** Stern–Volmer plot with different metal ions in THF–water (8:2, v/v) ( $\lambda_{\text{exc}} = 315$  nm).



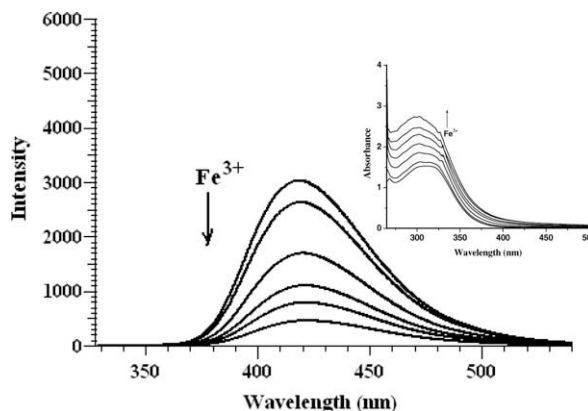
**Figure 3.** Fluorescence spectral changes of **1** ( $4.99 \times 10^{-2}$  mg/ml) with different metal ions (up to  $12.32 \times 10^{-5}$  M) in THF-water (8:2, v/v) ( $\lambda_{exc} = 315$  nm).

petitive metal ions, similar fluorescence quenching with  $Fe^{3+}$  ion was noticed. In addition, the quenching of fluorescence resulting from the addition of  $Fe^{3+}$  ion was not influenced by the subsequent addition of coexistent metal ions. Thus the results in the present study indicate that the polymer **1** reveals a significant selectivity toward  $Fe^{3+}$  over other surveyed metal ions. Polymer **1** might have a varying number of binding pockets constructed by both the 1-naphthylamine-N donor and the main chain proximal -OH groups. This site is expected to chelate strongly the smallest size  $Fe^{3+}$  ion among the other competitive metal ions as evidenced from the sizable increase in absorbance at  $\lambda_{max} = 315$  nm with the concentration of  $Fe^{3+}$  ions in UV-vis spectroscopy (Fig. 1: inset). This electron-deficient metal chelate moiety probably acts as a quencher for the naphthylamine fluorescence demonstrating chelation-enhanced fluorescence effect (OFF state) toward more oxidizing paramagnetic  $Fe^{3+}$  ion<sup>12,7c</sup> as proposed in Figure 4 as well as the absorbance effect of  $Fe^{3+}$  ion.<sup>13</sup>

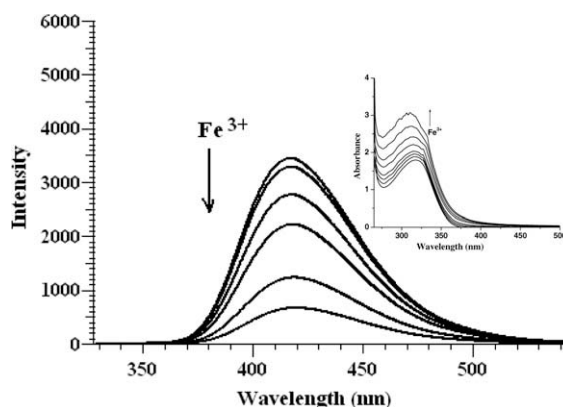
To examine the role of two proximal -OH groups in the chelation-enhanced fluorescence effect, model compounds **2** and **3** were undertaken in the study. A clear indication of binding of  $Fe^{3+}$  ion came from the UV-vis titration experiments of **2** (inset of Fig. 5) and **3** (inset Fig. 6) with  $Fe^{3+}$  ion where also identical trend of hyperchromic shift at 309 and 318 nm for **2** and **3**, respectively, was observed. We also noticed that the addition of  $Fe^{3+}$  to the solution of **2** induced significant fluorescence quenching (Fig. 5). On the contrary, addition of  $Fe^{3+}$  to the solution of **3** caused smaller decrease in emission (Fig. 6). These observations revealed that although **2** and **3** have the naphthylamine-N donor site, their emission behaviors toward  $Fe^{3+}$  are dramatically less compared to **1** and in particular, it is true for model compound **3**, which lacks two -OH groups. Thus this study demonstrates that the presence of -OH group is critically important for the tight chelation of metal ion which in turn activates the quenching process. Based on the fluo-



**Figure 4.** Suggested fluorescence quenching mechanism of **1** for  $Fe^{3+}$  ion.

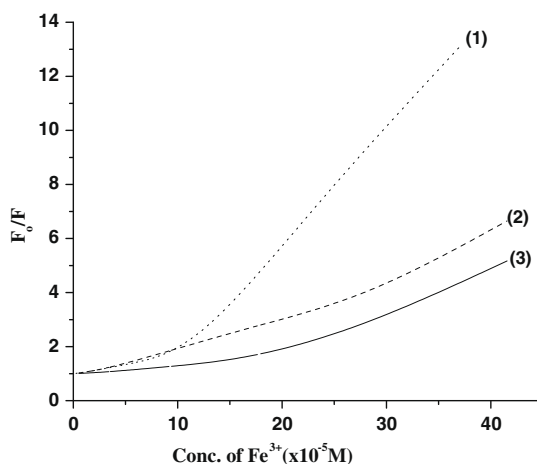


**Figure 5.** Fluorescence spectral changes of **2** ( $3.84 \times 10^{-4}$  M) with different concentrations of  $Fe^{3+}$  ion (up to  $4.16 \times 10^{-4}$  M) in THF-water (8:2, v/v) ( $\lambda_{exc} = 309$  nm); inset: UV-vis spectral change.

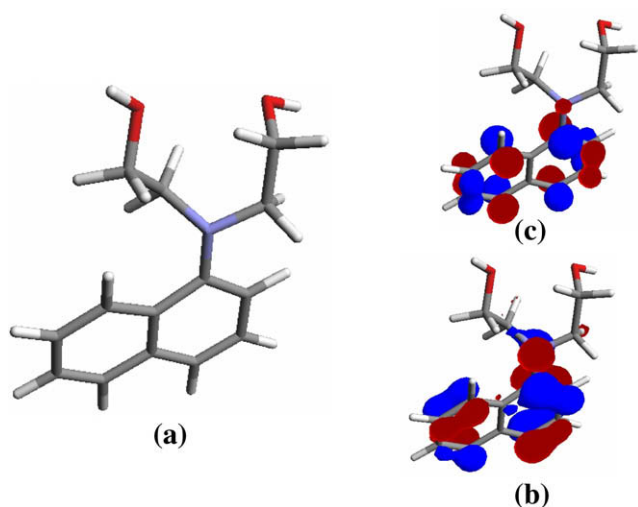


**Figure 6.** Fluorescence spectral changes of **3** ( $3.93 \times 10^{-4}$  M) with different concentrations of  $Fe^{3+}$  ion (up to  $4.16 \times 10^{-4}$  M) in THF-water (8:2, v/v) ( $\lambda_{exc} = 318$  nm); inset: UV-vis spectral change.

rescence titration of **1**, **2**, and **3** in THF-water (8:2, v/v) with  $Fe^{3+}$  ion, their Stern-Volmer plot (Fig. 7) was made demonstrating strongest response of **1**. These results indicate that polymer scaffold having varying number of -OH groups amplifies the fluorescence quenching toward  $Fe^{3+}$  ion.



**Figure 7.** Stern-Volmer plot of **1**, **2**, and **3** in the presence of  $Fe^{3+}$  ion in THF-water (8:2, v/v).



**Figure 8.** (a) AM1-optimized structure of **2** ( $E = -105.60$  au;  $d_{O-O} = 3.31$  Å); (b) HOMO; (c) LUMO.

An examination with the AM1-optimized structure<sup>14</sup> of **2** (Fig. 8) revealed the suitable orientation of two –OH groups along with 1-naphthylamine-N onto the coordination range. The HOMO of **2** is included on the n-orbital of 1-naphthylamine-N along with aromatic moiety. Therefore, the stronger chelation might be attributed to the crucial role of these –OH groups, which enabled Fe<sup>3+</sup> ion to penetrate more deeply into the binding pocket and thus gave the stronger perturbation of the electronic structure (HOMO) of the 1-naphthylamine moiety and fluorescence sensitivity.

In summary, novel epoxy-based polymer **1** represents an exciting new class of readily synthesized macromolecule, which is Fe<sup>3+</sup> ion-selective chemosensor over other physiologically and environmentally important metal ions. We anticipate that fluorescent macromolecule of this type having well-defined structure would be most welcome in the field of sensory systems based on the transduction of recognition events on the binding site (naphthylamine-N and –OH groups) into the fluorescent property of the naphthylamine units. In addition, the greater processing ability of polymers (i.e., into films, etc.) compared to that of small molecules is another possible advantage of this system. The macromolecular design of fluorophores effective for the detection of other metal ions is currently under progress in our laboratory.

## Acknowledgment

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- Polymer 1:** Diglycidyl ether of bisphenol-A (1.0 g, 2.63 mmol) and 1-naphthylamine (0.377 g, 2.63 mmol) were homogeneously mixed under slow heating and polymerized at 95–100 °C for 30 h. The product was dissolved in 1,4-dioxan and precipitated with plenty of water. Precipitate was collected and vacuum dried at 60 °C for 24 h. FT-IR (KBr):  $\nu_{\max} = 3396, 3048, 2964, 2869, 1601, 1512, 1447, 1387, 1291, 1248, 1181, 1041, 835, 768, 562$  cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.42 (br s, H<sup>f</sup>), 8.35 (br s, H<sup>g</sup>), 7.82 (br s, H<sup>f</sup>), 7.62 (br s, H<sup>g</sup>), 7.43–7.41 (br m, H<sup>d,h,i</sup>), 7.04 (br s, H<sup>b</sup>), 6.68 (br s, H<sup>c</sup>), 4.18–4.13 (br m, H<sup>p</sup>), 3.97–3.87 (br m, H<sup>q</sup>), 3.49–3.33 (m, H<sup>r</sup>), 3.19 (br s, –OH), 1.62 (s, H<sup>a</sup>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  156.40, 147.44, 143.65, 135.13, 130.81, 128.60, 127.79, 126.17, 125.66, 124.93, 123.44, 121.16, 120.48, 118.10, 114.08, 113.96, 70.31, 68.81, 68.27, 58.14, 50.25, 44.83, 41.73, 31.06. GPC (using polystyrene and THF):  $M_w = 28,300$ , PDI = 1.72; Anal. Calcd for (C<sub>49</sub>H<sub>53</sub>NO<sub>7</sub>)<sub>n</sub>: C, 78.08; H, 7.03; N, 1.85. Found: C, 77.90; H, 6.99; N, 1.90.
- Model compound 2:** A suspension of 1-naphthylamine (0.5 g, 3.49 mmol), 2-chloroethanol (2.25 g, 27.97 mmol), and calcium carbonate (1.74 g, 17.48 mmol) in 30 ml water was refluxed for 36 h, and the filtrate was extracted with dichloromethane. The organic phase was dried over anhyd Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed in vacuo to get the crude product, which was purified by column chromatography (silica gel, petroleum ether/EtOAc 85:15) to obtain pure product (60–65%). FT-IR (KBr):  $\nu_{\max} = 3368, 2923, 2852, 1634, 1592, 1574, 1397, 1067, 1039$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.40 (br s, H<sup>g</sup>), 7.85 (d, 1H<sup>d</sup>,  $J = 10$  Hz), 7.65 (d, 1H<sup>c</sup>,  $J = 10$  Hz), 7.50 (m, 2H<sup>b,e</sup>), 7.42 (t, 1H<sup>f</sup>,  $J = 7$  Hz), 7.35 (d, 1H<sup>a</sup>,  $J = 5$  Hz), 3.69 (s, 4H), 3.43 (s, 4H), 1.55 (s, –OH). Anal. Calcd for C<sub>14</sub>H<sub>17</sub>NO<sub>2</sub>: C, 72.72; H, 7.35; N, 6.06. Found: C, 70.72; H, 7.32; N, 6.03.
- Model compound 3:** A solution of 1-naphthylamine (0.2 g, 1.39 mmol), *n*-butyl bromide (0.958 g, 6.99 mmol), and Et<sub>3</sub>N (1.39 mmol) in dry THF was placed in a round-bottomed flask under nitrogen atmosphere and refluxed for 72 h. The solvent was evaporated and the residue was treated with water and extracted with dichloromethane. The organic phase was dried over anhyd Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed in vacuo to get the crude product, which was purified by column chromatography (silica gel, petroleum ether/EtOAc 94:6) to obtain pure product (40–45%). FT-IR (KBr):  $\nu_{\max} = 2957, 2930, 2861, 2821, 1575, 1462, 1378, 1084$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.29 (d, 1H<sup>g</sup>,  $J = 10$  Hz), 7.79 (d, 1H<sup>d</sup>,  $J = 10$  Hz), 7.53 (d, 1H<sup>c</sup>,  $J = 10$  Hz), 7.45 (m, 2H<sup>b,e</sup>), 7.40 (t, 1H<sup>f</sup>,  $J = 7$  Hz), 7.15 (d, 1H<sup>a</sup>,  $J = 7$  Hz), 3.12 (t, 4H,  $J = 7$  Hz), 1.47 (m, 4H), 1.28 (m, 4H), 0.85 (m, 4H). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>N: C, 84.70; H, 9.80; N, 5.49. Found: C, 84.69; H, 9.79; N, 5.48.
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- Energy optimization was performed by using ArgusLab 4.0, Mark A. Thompson, Planaria Software LLC, Seattle, WA (<http://www.arguslab.com>).