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Thermotropic liquid crystals of 1*H*-imidazole amphiphiles showing hexagonal columnar and micellar cubic phases

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Abstract—The linear and polycatenar type 1*H*-imidazole amphiphiles showing a strong self-assembly tendency to build various supramolecular structures in bulk were synthesized by the esterification reaction of 4′-alkyloxy phenols (for **1**–**4**) and hydroxyphenyl trialkyloxybenzoates (for **5**–**7**) with 4-chlorocarbonyl imidazole. The linear 1*H*-imidazole amphiphiles formed thermotropic smectic phases, but compound **4** with an ethyl group instead of hydrogen on 1*N* did not show a mesophase. The polycatenar type 1*H*-imidazole amphiphiles (**5**–**7**) formed thermotropic hexagonal columnar and cubic phases. A phase transition was observed from a columnar phase to a cubic phase as the temperature increased on heating, and vice versa on cooling. In the POM study for compounds **5**–**7**, optically isotropic phases first appeared on cooling from the isotropic melts, and then birefringent mesophases with a nonspecific texture appeared on further cooling. The X-ray analysis shows that the optically isotropic phases were very likely micellar cubic phases with *Pm*3*n* symmetry. The birefringent phases were confirmed as hexagonal columnar phases.

Amphiphilic molecules have been widely used as a building block for the synthesis of supramolecular materials.[1–5] They are self-assembled into various supramolecular structures such as a micelle, ellipsoid, cylinder and vesicle in aqueous or organic solutions. There have been also reported highly ordered liquid crystalline phases of the amphiphiles in solutions as well as in bulk.[6,7] We previously reported the self-assembly of 1*H*-imidazole amphiphiles in solution, forming organogels, micelles or lyotropic liquid crystals depending on their molecular structures. For example, the linear amphiphiles having an imidazole head connected to a hydrophobic alkyloxyphenyl group through an ester linkage formed organogels.[8,9] The polycatenar 1*H*-imidazole amphiphiles formed lyotropic liquid crystals showing columnar hexagonal structures and bundles at the surface of silicon. This strong tendency of 1*H*-imidazole amphiphiles to self-assemble in solution is largely indebted to its capability of acting as both a proton donor and acceptor in forming hydrogen bonding. In biological systems, imidazole and its derivatives are known to play important roles as the proton donor and/or acceptor.[10–12] Recently, ionic liquid crystals based on imidazolium salts gained much attention as reaction solvents.[13–16]

In this Letter, we studied on thermotropic liquid crystalline properties of 1*H*-imidazole amphiphiles. Very interestingly, polycatenar type amphiphiles with a 1*H*-imidazole head show transitions of hexagonal columnar phases to cubic phases on heating and vice versa on cooling, while linear amphiphiles show smectic phases. Cubic phases[17–19] represent highly ordered supramolecular arrangements with optically isotropic properties. Cubic phases have been frequently found in lyotropic liquid crystalline systems, comprising lipid (or surfactant) and solvent, but relatively few compounds with thermotropic cubic mesophases (e.g., polyhydroxy derivatives, folic acid derivatives, cone-shaped monodendrons and rod-coil molecules) are known.[19–23] Discotic liquid crystals are attractive due to their potential applications in devices such as photovoltaic solar cells[24,25] and electro-luminescent displays.[26] Typical discotic liquid crystalline compounds consist of disk-like aromatic rings[27,28] as a core and peripheral alkyl chains but there have been also reported discotic liquid crystals formed by supramolecular assemblies of molecules other than discotic ones.[29–31]

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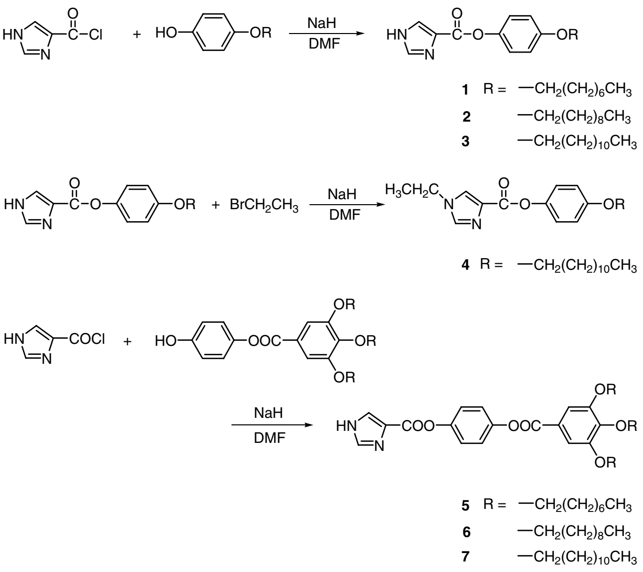
1*H*-Imidazole amphiphiles were prepared according to our previous reports.[8,9] Linear 1*H*-imidazole amphiphiles (**1**–**3**) were synthesized by the esterification reaction of 4′-alkyloxy phenol with 4-chlorocarbonyl imidazole under basic conditions.[32] For comparison, compound **4** was prepared, where 1*N* of the imidazole head was blocked by ethyl group.[33] Polycatenar 1*H*-imidazole amphiphiles (**5**–**7**) were obtained by the esterification reaction of hydroxyphenyl trialkyloxybenzoates with 4-chlorocarbonyl imidazole (Scheme 1).[34] The structures were fully characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

The thermotropic properties of compounds **1**–**7** were investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). In the DSC analysis, compounds **1**–**3** show monotropic mesophases. Compound **2** show a crystal to crystal transition at 128 °C with an enthalpy value of 7.9 J/g and a melt transition at 155 °C with an enthalpy value of 52.6 J/g on heating. In the subsequent cooling cycle, an isotropic to liquid crystal transition at 132 °C with an enthalpy value of 23.0 J/g and a liquid crystal to crystal transition at 111 °C with an enthalpy value of 26.6 J/g occurred. In POM analysis, a birefringent phase was observed from 132 °C to 111 °C on cooling (Fig. 1a). Compounds **1** and **3** also show monotropic transitions similar to those of compound **2**. However, compound **4** with an ethyl group instead of hydrogen on 1*N* did not show a mesophase, supporting the idea that hydrogen bonding is critical in these systems. Polycatenar compounds **5**–**7** having one more phenyl group and two more side chains, compared to compounds **1**–**3**, exhibited both hexagonal columnar and cubic phases. A phase transition was observed from a columnar phase to a cubic phase as the temperature increased on heating, and vice versa on cooling. Compound **7** show a crystal to hexagonal columnar phase transition at 48 °C with an enthalpy value of 3.6 J/g, a hexagonal columnar phase to cubic phase transition at 80 °C with an enthalpy value of 14.0 J/g, and a cubic phase to isotropic liquid transition at 114 °C with an enthalpy value of 0.42 J/g on heating. In the subsequent cooling cycle, an isotropic to cubic phase transition at 112 °C with an enthalpy value of 0.05 J/g, a cubic phase to hexagonal columnar phase transition at 86 °C with an enthalpy value of 10.4 J/g, and a hexagonal columnar phase to crystal transition at 24 °C with an enthalpy value of 0.14 J/g occurred. Compounds **5** and **6** having shorter alkyl chains also showed enantiotropic transitions similar to those of compound **7**. Phase transition temperatures and corresponding enthalpy values for compounds **1**–**3** and **5**–**7** are given in Table 1. In the POM study, only optically isotropic phases appeared initially on cooling from the isotropic melts of compounds **5**–**7**, which is characteristic of a cubic structure. Birefringent mesophases with a nonspecific texture began to form on further cooling. A typical POM image obtained from **7** is shown in Figure 1b.



Scheme 1.

The structures of the liquid crystals of **1**–**3** were investigated by using an X-ray diffraction technique. In the small angle region, only one sharp reflection peak corresponding to the *d* spacing of 31.5 Å (for **1**), 33.4 Å (for **2**) and 34.5 Å (for **3**) appeared (Fig. 2).

Since the lengths of the molecules were calculated to be 19.9 Å (for **1**), 22.0 Å (for **2**) and 24.4 Å (for **3**), respectively, using a simple molecular modeling (MM2) method, it seems that they existed in a dimer form with

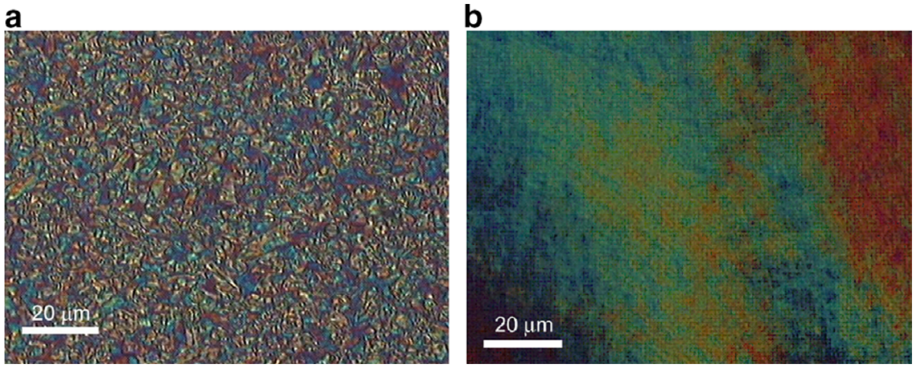


Figure 1. Polarizing optical micrographs of (a) compound **2** and (b) **7** obtained at 130 °C and 65 °C, respectively, on cooling at a rate of 5 °C min^{-1}.

Table 1. Phase transition temperatures and enthalpy values (in parentheses) of 1*H*-imidazole amphiphiles as determined by DSC (scan rate: 5 °C min^{-1}) or POM[a]

Compound	Phase transition temperature (°C) and Δ H (J g^{-1})	
	2nd heating	2nd cooling
1	Cr 125 (5.4) Cr 154 (51.4) I	I 131 (13.4) Sm 110 (27.8) Cr
2	Cr 128 (7.9) Cr 155 (52.6) I	I 132 (23.0) Sm 111 (26.6) Cr
3	Cr 120 (17.4) Cr 146 (41.8) I	I 134 (25.3) Sm 112 (27.9) Cr
5	Cr 35 (3.9) Col_h 95 (17.7) Cub 120 (0.04) I	I 115 (0.01) Cub 94 (7.9) Col_h 23 (0.04) Cr
6	Cr 23 (2.0) Col_h 82 (13.1) Cub 115 (0.02) I	I 114[b] Cub 91 (7.1) Col_h 27 (0.06) Cr
7	Cr 48 (3.6) Col_h 80 (14.0) Cub 114 (0.42) I	I 112 (0.05) Cub 86 (10.4) Col_h 24 (0.14) Cr

[a] Abbreviations: Cr = crystalline; Sm = smectic; I = isotropic; Col_h = hexagonal columnar; Cub = cubic mesophase.
[b] Determined by POM.

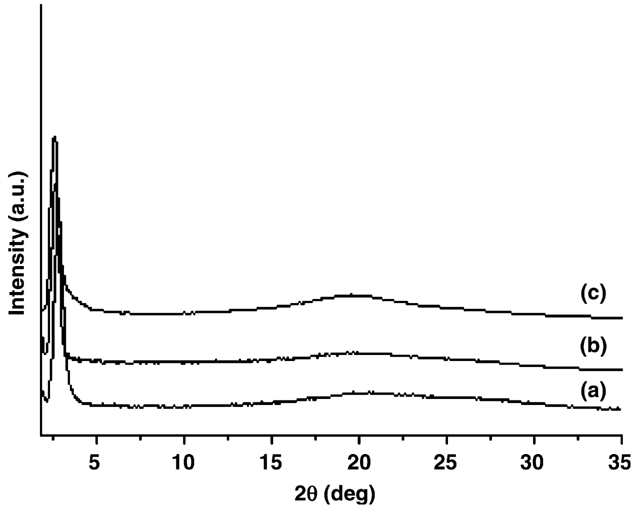


Figure 2. X-ray diffractograms for the smectic phases of (a) compound **1**, (b) compound **2** and (c) compound **3** obtained at 120 °C on the second cooling.

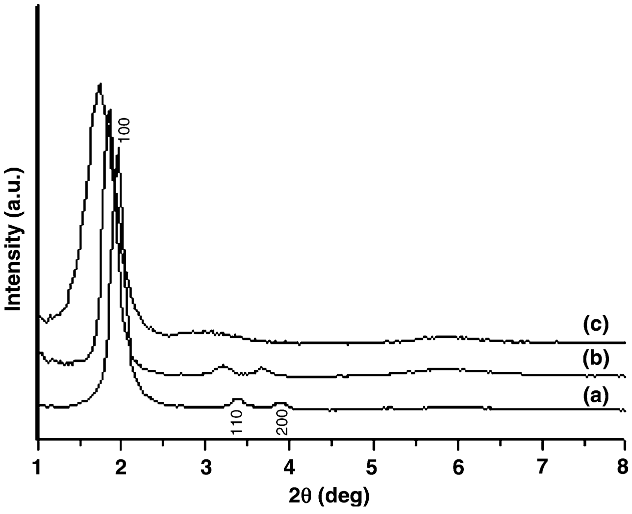


Figure 3. X-ray diffractograms for the hexagonal columnar phases of (a) compound **5**, (b) compound **6** and (c) compound **7** obtained at 40 °C on cooling.

hydrogen bonding between imidazole moieties, forming smectic structures. The observed layer distances were smaller than twice the molecular lengths, indicating either a tilted arrangement of the molecules or interdigitation of the alkyl chains.

The birefringent phases of polycatenar 1*H*-imidazole amphiphiles **5**–**7** were confirmed as columnar hexagonal phases. In the small angle X-ray diffractograms obtained at 40 °C on cooling, three reflection peaks corresponding to the *d* spacings of 46.0, 26.7 and 23.4 Å (for **5**) and 47.4, 27.8 and 23.6 Å (for **6**) and 50.7, 28.8 and 25.4 Å (for **7**) appeared (Fig. 3). These reflections are indexed in sequence as (100), (110) and (200) of a hexagonal columnar lattice with the lattice parameter of $a = 53.1$ (for **5**), 54.8 (for **6**) and 58.5 (for **7**). In addition, a diffuse halo is observed in the wide-angle region at 4.55 (for **5**), 4.52 (for **6**) and 4.39 Å (for **7**).

The lengths of the molecules were calculated to be 25.8 Å (for **5**), 28.7 Å (for **6**) and 31.0 Å (for **7**), respectively, using the MM2 method, which were close to the radii of the corresponding disks determined by X-ray analysis. Judging from these results and the structural motif of a polycatenar molecule, it is very likely that the molecules are arranged in a disk to form a longer mesogen via hydrogen bonding between successive imidazole moieties as shown in Figure 5 (left).[8,9,35] Chain structures of hydrogen bonded imidazole molecules have been found in the crystal state and in the solution state.[8,31,35] Assuming a density of $\rho = 1\ g\,cm^{-3}$, the number (n) of molecules arranged side by side in a single slice of the columns with a thickness (h) of approximately 0.45 nm was estimated according to Eq. 1.[36]

$$n = (a^2)\sqrt{3}/2h(N_A/M)\rho \qquad (1)$$

The parameter a is the hexagonal lattice parameter, N_A the Avogadro constant and M the molecular mass. The number of molecules in a disk at the thermotropic columnar state was calculated to be about 9–10.

The X-ray analysis shows that the optically isotropic phases were very likely micellar cubic phases with *Pm*3*n* symmetry (Fig. 4).[19–22] In the small angle X-ray diffractogram of compound **5** obtained at 100 °C on cooling, two reflections corresponding to *d* spacings of 41.0 and 36.2 Å were observed. These reflections are indexed in sequence as (200) and (210) of a cubic phase with a lattice parameter of $a = 82.0$ Å. Four reflections

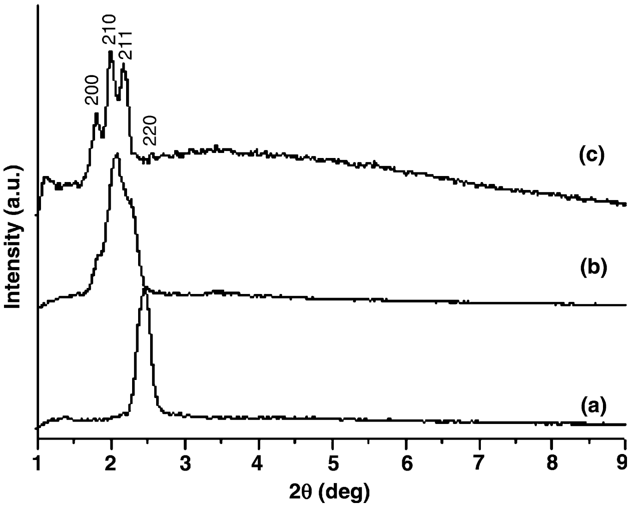


Figure 4. X-ray diffractograms for the cubic phases of (a) compound **5** obtained at 100 °C, (b) compound **6** obtained at 110 °C and (c) compound **7** obtained at 95 °C on cooling.

corresponding to d spacings of 47.7, 42.2, 39.2 and 33.6 Å for **6** at 110 °C and 49.0, 44.3, 40.9 and 34.7 Å for **7** at 95 °C appeared. The relative positions of these reflections are $\surd 4$, $\surd 5$, $\surd 6$ and $\surd 8$, which is in good agreement with the (2 0 0), (2 1 0), (2 1 1) and (2 2 0) reflections of cubic phase with $Pm3n$ symmetry with lattice constants of 95.4 Å for **6** and 98.0 Å for **7**. Assuming a density of $\rho = 1\ \mathrm{g\,cm^{-3}}$, the number ($n_{\mathrm{cell}}$) of molecules in each unit cell of the cubic lattice was estimated according to Eq. 2.[36]

$$n_{\mathrm{cell}} = V_{\mathrm{cell}}(N_{\mathrm{A}}/M)\rho \qquad (2)$$

The parameter V_{cell} is the volume of unit cell of cubic lattice, N_{A} the Avogadro constant and M the molecular mass. The number of molecules in each unit cell of the cubic lattice (n_{cell}) at the cubic state is 479 for **5**, 673 for **6** and 658 for **7**.

Since the molecular lengths of the amphiphiles were much smaller than the lattice parameters (e.g., the cubic phase of **7** has a lattice parameter of $a = 98.0$ Å, while the calculated molecular length is 31.0 Å), the possibility of the arrangement of spherical micelles in a primitive cubic cell were excluded. Under similar circumstances, Fontell et al. and Tschierske et al. proposed a thermotropic micellar cubic phase in which eight short rod-like aggregates (*inverted micelles*) formed a cubic unit cell ($Pm3n$). One of these rod-like micelles is located at each corner of the unit cell, one in the center and the other two on each face of the unit cell.[23,37,38] We presume that the polycatenar 1*H*-imidazole amphiphiles reported here also formed the cubic lattices built up by eight short rod-like micelles with each micelle consisting of approximately 60 (for **5**), 84 (for **6**) and 82 (for **7**) individual molecules (Fig. 5 (right)). The $Pm3n$ lattice seems to be the generally favoured packing motif of rod-like or spherical micelles as it provides a dense packing with minimum interfaces.[20]

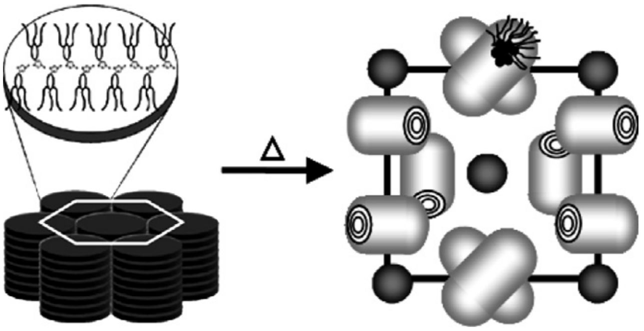


Figure 5. Schematic representation of a hexagonal columnar to cubic phase transition.

In summary we prepared the linear and polycatenar type 1*H*-imidazole amphiphiles where an imidazole head was connected to a hydrophobic alkyloxyphenyl or a hydroxyphenyl trialkyloxybenzoate group through an ester linkage. The polycatenar 1*H*-imidazole amphiphiles formed thermotropic liquid crystals having hexagonal columnar and cubic structures. The transitions from a columnar mesophase to a cubic phase were observed as the temperature increased on heating, and vice versa on cooling. The linear type 1*H*-imidazole amphiphiles formed thermotropic smectic phases. When hydrogen on 1*N* of an imidazole ring was substituted by an ethyl group, the compound did not show liquid crystal phase, strongly suggesting that the capability of a 1*H*-imidazole to act as a proton donor as well as an acceptor in forming hydrogen bonding plays a major role in its self-assembly.

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32. Compounds **1**–**3**: These compounds were prepared according to our previous report.[8] A typical procedure is as follows: 4-Imidazole carboxylic acid (1 g, 9 mmol) in benzene (10 mL) was stirred at room temperature, and then thionyl chloride (10 mL) dissolved in benzene (10 mL) was added slowly. The mixture was refluxed for 10 h. After evaporation, the product (4-chlorocarbonylimidazole) was dried and used for the next reaction without further purification. To a solution of 4′-octyloxy phenol (1 g, 4.40 mmol) and sodium hydride (0.13 g, 4.84 mmol) in DMF (50 mL) was added 4-chlorocarbonylimidazole (0.83 g, 4.84 mmol) under nitrogen. The reaction mixture was stirred for 24 h at 90 °C. After removal of precipitates by filtration, the filtrates were concentrated to dryness by evaporation under reduced pressure. The product (compound **1**) was isolated by column chromatography on silica gel (THF/*n*-hexane = 3/1); yield 0.93 g (60%). ^{1}H NMR (300 MHz, DMSO): $\delta = 12.82$ (s, 1H, NH), 8.03, 7.88 (s, 2H, imidazole ring protons), 7.10, 6.95 (dd, 4H, ArH), 3.96 (t, 2H, ArOCH$_2$), 1.73–1.28 (m, 12H, CH$_2$), 0.85 (t, 3H, CH$_3$). ^{13}C NMR (75 MHz, DMSO): δ 164.4, 139.1, 133.6, 120.5, 117.2, 85.3, 75.1, 74.6, 65.6, 31.7, 29.0, 28.7, 22.9, 20.0, 14.5. IR (KBr pellet, cm^{-1}): 3141, 3011, 2920, 2850, 2654, 2593, 1728, 1508, 1449, 1336, 1199, 979. Compound **2**: Yield 0.92 g (55%). ^{1}H NMR (300 MHz, DMSO): δ 12.82 (s, 1H, NH), 8.03, 7.88 (s, 2H, imidazole ring protons), 7.10, 6.95 (dd, 4H, ArH), 3.96 (t, 2H, ArOCH$_2$), 1.73–1.28 (m, 16H, CH$_2$), 0.85 (t, 3H, CH$_3$). ^{13}C NMR (75 MHz, DMSO): δ 164.4, 139.1, 133.6, 120.5, 117.2, 85.3, 75.1, 74.6, 65.6, 32.2, 29.6, 29.5, 29.3, 28.7, 23.1, 20.0, 14.5. IR (KBr pellet, cm^{-1}): 3141, 3011, 2920, 2851, 2654, 2593, 1729, 1508, 1447, 1338, 1199, 977. Compound **3**: Yield 0.93 g (52%). ^{1}H NMR (300 MHz, DMSO): δ 12.80 (s, 3H, NH), 8.05, 7.88 (s, 2H, imidazole ring protons), 7.09, 6.96 (dd, 4H, ArH), 3.96 (t, 2H, ArOCH$_2$), 1.70-1.25 (m, 20H, CH$_2$), 0.86 (t, 3H, CH$_3$). ^{13}C NMR (75 MHz, DMSO): δ 164.2, 138.9, 133.4, 120.3, 117.0, 85.0, 74.8, 74.4, 65.4, 32.1, 29.8, 29.7, 29.5, 29.3, 29.1, 28.5, 22.9, 19.8, 14.3. IR (KBr pellet, cm^{-1}): 3152, 3010, 2917, 2851, 2654, 2585, 1733, 1507, 1446, 1342, 1199, 982.

33. Compound **4**: This compound was prepared according to our previous report.[8] To a solution of compound **3** (0.2 g, 0.49 mmol) and sodium hydride (0.015 g, 0.54 mmol) in DMF (15 mL) was added 1-bromoethane (0.15 mL, 1.47 mmol) under nitrogen. The reaction mixture was stirred for 24 h at 90 °C. After removal of precipitates by filtration, the filtrates were concentrated to dryness by evaporation under reduced pressure. The product was isolated by column chromatography on silica gel (EA/*n*-hexane = 2/1); yield 0.19 g (90%). ^{1}H NMR (300 MHz, DMSO): δ 7.88, 7.58 (s, 2H, imidazole ring protons), 7.10, 6.90 (dd, 4H, ArH), 4.07 (q, 2H, N–CH$_2$), 3.94 (t, 2H, ArOCH$_2$), 2.17 (t, 3H, N–CH$_2$CH$_3$), 1.75–1.27 (m, 20H, CH$_2$), 0.88 (t, 3H, CH$_3$). ^{13}C NMR (75 MHz, DMSO): δ 164.5, 139.3, 133.4, 120.4, 117.2, 85.1, 74.8, 74.4, 65.4, 39.9, 32.1, 29.8, 29.7, 29.5, 29.3, 29.1, 28.5, 22.9, 19.8, 16.4, 14.3. IR (KBr pellet, cm^{-1}): 3101, 2923, 2852, 1740, 1506, 1386, 1245, 1191, 1171, 1080, 966.

34. Compounds **5**–**7**: These compounds were prepared according to our previous report.[9] A typical procedure is as follows. To a solution of 4-hydroxyphenyl 3,4,5-tris(*n*-octan-1-yloxy)benzoate[9] (1 g, 1.7 mmol) in DMF (50 mL) was added sodium hydride (0.05 g, 2.0 mmol). After stirring for 1 h at room temperature, 4-chlorocarbonyl imidazole (1.24 g, 7.4 mmol) was added. The solution was stirred for 24 h at 90 °C. After filtration and evaporation, the product (compound **5**) was isolated by column chromatography on silica gel (THF/*n*-hexane = 2/1 v/v) and further purified by recrystallization from THF/*n*-hexane; (65 % yield). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.92, 7.84 (s, 2H, imidazole ring protons), 7.41 (s, 2H, ArH), 7.27 (dd, 4H, ArH), 4.05 (t, 6H, ArOCH$_2$), 1.29–1.86 (m, 36H, CH$_2$), 0.88 (t, 9H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 165.47, 161.30, 153.22, 148.69, 148.28, 143.41, 138.10, 123.80, 123.07, 122.98, 108.87, 73.87, 69.53, 32.11, 32.03, 31.12, 30.57, 29.72, 29.56, 29.53, 29.49, 26.31, 26.26, 22.90, 22.87, 13.80. IR (KBr pellet, cm^{-1}): 3113, 3078, 2925, 2663, 2598, 1732, 1504, 1336, 1178, 1127, 976. Compound **6**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.92, 7.84 (s, 2H, imidazole ring protons), 7.41 (s, 2H, ArH), 7.26 (dd, 4H, ArH), 4.05 (t, 6H, ArOCH$_2$), 1.29–1.86 (m, 48H, CH$_2$), 0.87 (t, 9H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 165.44, 160.82, 153.22, 148.70, 148.22, 143.42, 138.08, 123.78, 123.03, 122.96, 108.86, 73.85, 69.53, 32.15, 32.12, 30.56, 29.94, 29.90, 29.88, 29.84, 29.79, 29.61, 29.55, 29.52, 26.30, 26.27, 22.90, 14.31. IR (KBr pellet, cm^{-1}): 3113, 3068, 2852, 2666, 2600, 1735, 1502, 1338, 1180, 1122, 976. Compound **7**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.92, 7.84 (s, 2H, imidazole ring protons), 7.41 (s, 2H, ArH), 7.26 (dd, 4H, ArH), 4.05 (t, 6H, ArOCH$_2$), 1.29–1.86 (m, 60H,

CH_2), 0.87 (t, 9H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.45, 160.65, 153.22, 148.71, 148.20, 143.43, 138.06, 123.77, 123.02, 122.96, 108.86, 73.85, 69.53, 32.15, 32.13, 30.57, 29.94, 29.91, 29.87, 29.85, 29.79, 29.62, 29.57, 29.53, 26.31, 26.28, 22.90, 14.3. IR (KBr pellet, cm^{-1}): 3113, 3078, 2852, 2664, 2598, 1733, 1504, 1337, 1177, 1121, 976.

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