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Synthesis, optical and thermal studies of dendritic architectures with chalcone surface groups

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ABSTRACT

Dendritic architectures bearing three, six, and twelve chalcone units in the periphery are synthesized through convergent approaches. Absorption, emission, photoisomerization, and thermal properties of the chalcone-based dendritic architectures are also studied.

Dendrimers are highly branched monodisperse synthetic organic spherical macromolecules. Due to their multifunctional nature, dendrimers offer innumerable applications in biological and material sciences.[1,2] Photocrosslinkable,[3–5] photoswitchable,[6,7] and water soluble[8] dendrimers have been widely reported. α,β-Unsaturated compounds are important precursors for many potentially bioactive compounds, for example, hydroxy chalcones are the most important nucleus abundantly present in plants.[9] Chalcone derivatives are known to exhibit excellent cytotoxic,[10] antioxidant,[11] antibiotic,[12] and anticancer[13] activities. Similarly, chalcone core units are used in redox activity[14] and for the synthesis of nonlinear optical materials[15] and fluorescent dyes.[16]

Among many promising photosensitive groups, chalcones are often used for synthesizing photocrosslinkable polymers due to their high sensitivity to UV radiation and high cross-linking efficiency.[17] Though a few reports on the synthesis of dendritic architectures with chalcone moieties are available in the literature,[18] as well as from our laboratory,[19] extensive studies have not been carried out. In view of the emerging importance of chalcone dendrimers with respect to photoresponsive behavior, we report herein our synthesis, absorption, emission, photoisomerization, and thermal studies of aryl ether dendritic architectures **1** and **2** with three and six chalcone units and also dendritic architectures **3** and **4** containing six and twelve chalcone units, respectively.

Dendron **8** could be synthesized by either a one-step or a two-step procedure. Reaction of 1 equiv of dibromide **5**[20] with 2.1 equiv of **6**[21] in the presence of K_2CO_3 in CH_3CN under reflux for two days afforded dendron **8** in 83% yield.

However, in a two-step procedure, dibromide **5** was reacted with 2.1 equiv of **6** under similar conditions as mentioned earlier, but for 8 h, to give the acyl dendron **7** in 88% yield which was then deprotected using 2.0 equiv of KOH in ethanol under refluxing conditions for 3 h to give dendron **8** in 65% yield (Scheme 1). The ^{1}H NMR spectrum of dendron **8** displayed three sharp singlets at δ 5.18, δ 6.86, and δ 9.67 for two *O*-methylene, two *ortho* protons of the phenolic moiety, and one OH proton in addition to olefinic and aromatic protons. In the ^{13}C NMR spectrum, the *O*-methylene and carbonyl carbon appeared at δ 69.3 and δ 187.3 in addition to 14 aromatic carbons. The structure of dendron **8** was confirmed based on spectral and analytical data.[22]

In order to synthesize the dendrimers **1** and **2**, the tribromide **9**[23] was reacted with 3.0 equiv of **6** or **8** in the presence of K_2CO_3 in CH_3CN under refluxing conditions for two days to give dendrimers **1** and **2** in 95% and 73% yields, respectively (Scheme 2). The ^{1}H NMR spectrum of **1** displayed two sharp singlets at δ 2.50 and δ 5.23 for three identical sets of methyl and *O*-methylene protons in addition to olefinic and aromatic protons. In the ^{13}C NMR spectrum, the methyl, *O*-methylene, and carbonyl carbons appeared at δ 16.0, δ *65.2,* and δ 188.7 in addition to the aromatic carbons.

Similarly, dendrimers **3** and **4** were synthesized in 83% and 69% yields, respectively, from hexakis(bromomethyl)benzene **10**[23] and 6.0 equiv of **6** and **8** (Scheme 3). The ^{1}H NMR spectrum of **3** showed a sharp singlet at δ 5.34 for the twelve *O*-methylene protons in addition to olefinic and aromatic protons. In the ^{13}C NMR

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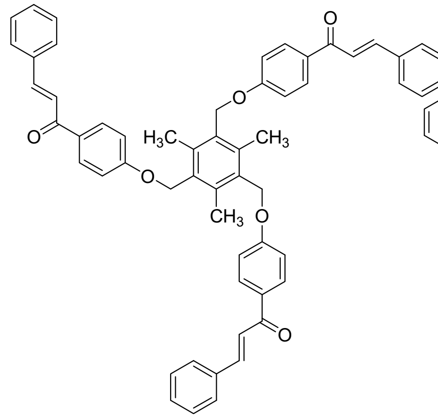

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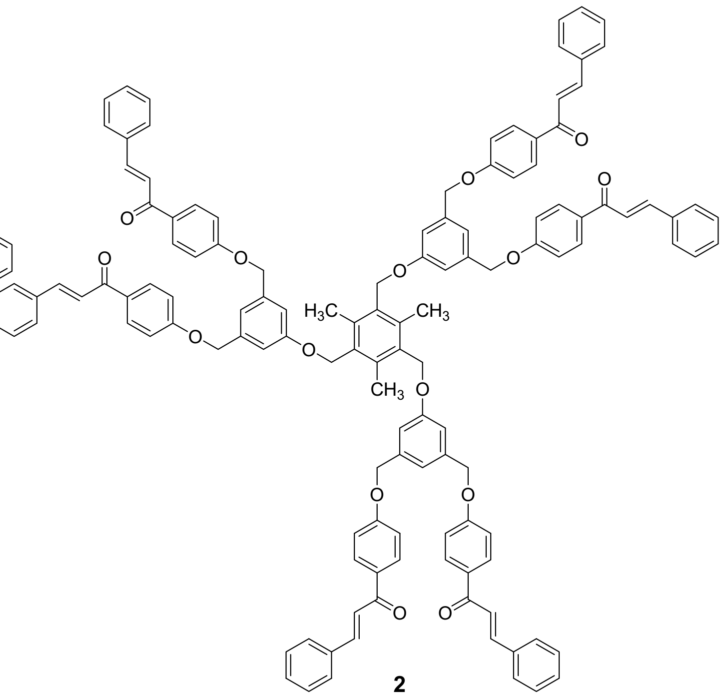

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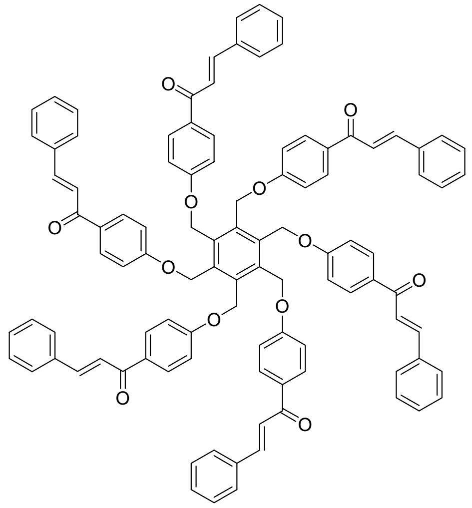

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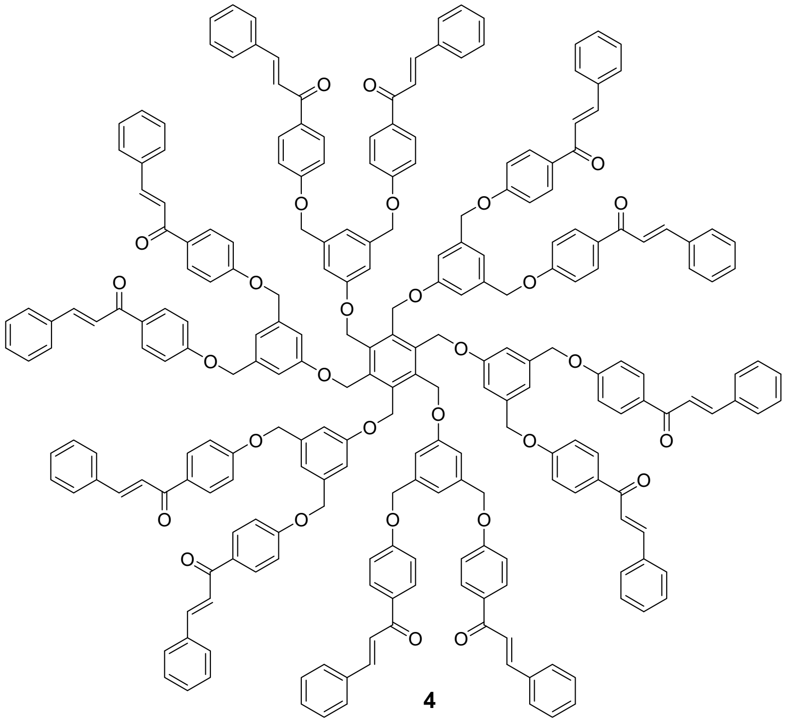
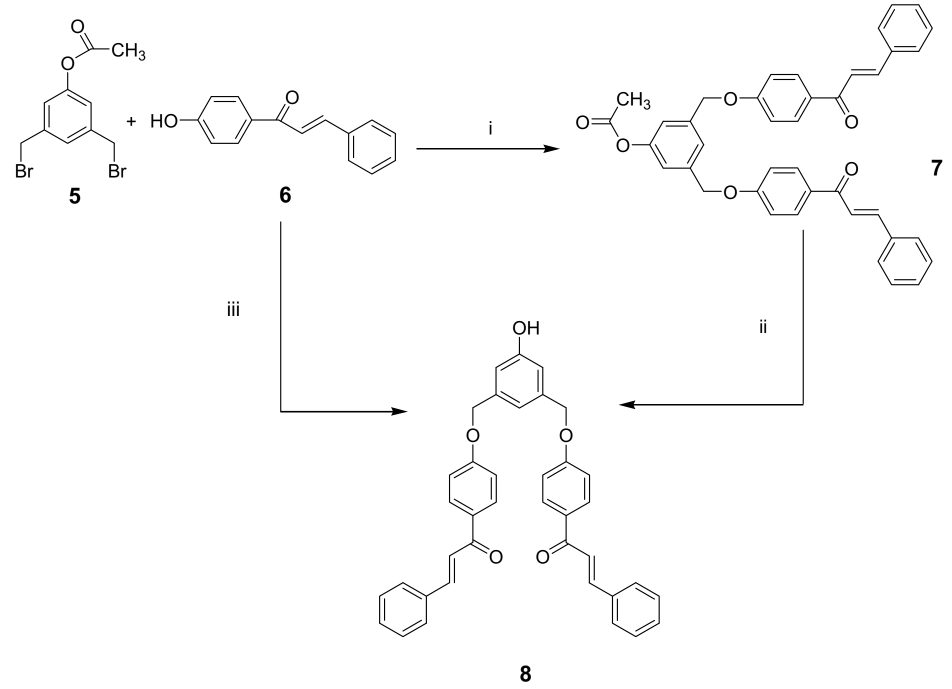


4

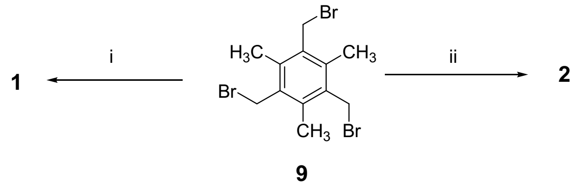
spectrum, the *O*-methylene and carbonyl carbons appeared at δ 63.9 and δ 188.5 and the aromatic carbons at δ 114.4 to δ 161.8. The structures of dendritic architectures **1**, **2**, **3**, and **4** were confirmed from spectroscopic and analytical data.[24–27]

The absorption and emission wavelengths of dendrimers **1**, **2**, **3** and **4** are given in Table 1. All the dendrimers exhibited an intense absorption band between 312 and 319 nm due to the presence of the chalcone chromophores. Dendrimer **4** showed a stronger absorbance than the dendritic architectures **1**, **2**, and **3** as the absorbance intensity is found to increase as the number of chalcone units in the dendritic architectures increases (Fig. 1).

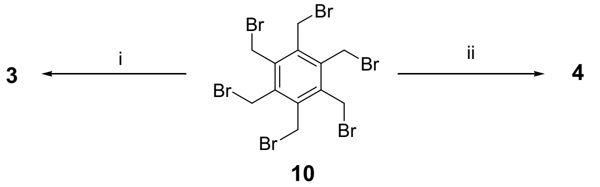
The fluorescence properties of dendrimers **1**, **2**, **3**, and **4** parallel the absorption spectra. All the dendrimers showed fluorescence maxima at 450 nm (λ_{exc}). Unlike in the absorption spectra, the emission spectra showed fluorescence quenching with increasing number of chalcone units[28] (Fig. 2), which was further confirmed from the fluorescence quantum yield (Φ_F). The fluorescence quantum yields of all the dendrimers were recorded using anthracene (0.2) in ethanol as an internal standard. The quantum yields of **1**, **2**, **3**, and **4** are 0.007, 0.005, 0.006, and 0.003, respectively, and indicate that the fluorescence intensity of the dendritic architectures decreases with increasing chalcone units (Table 1). Though



Scheme 1. Reagents and conditions: (i) K_2CO_3, CH_3CN, 8 h, reflux, **7** (88%); (ii) KOH, EtOH, 3 h, reflux **8** (65%); (iii) K_2CO_3, CH_3CN, 48 h, reflux, **8** (83%).



Scheme 2. Reagents and conditions: (i) 3.0 equiv of **6**, K_2CO_3, CH_3CN, 48 h, reflux, **1** (95%); (ii) 3.0 equiv of **8**, K_2CO_3, CH_3CN, 48 h, reflux, **2** (73%).



Scheme 3. Reagents and conditions: (i) 6.0 equiv of **6**, K_2CO_3, CH_3CN, 48 h, reflux, **3** (83%); (ii) 6.0 equiv of **8**, K_2CO_3, CH_3CN, 48 h, reflux, **4** (69%).

Table 1
Absorption and emission data and quantum yields of dendrimers **1**, **2**, **3**, and **4**

Dendrimer	UV–vis[a] λ_{max} (nm)	Emission[a] λ_{max} (nm)	Φ_F
1	312	430	0.007
2	316	440	0.005
3	315	446	0.006
4	319	450	0.003

[a] All spectra were recorded at 1×10^{-6} M in $CHCl_3$.

dendrimer **4** has the highest number of chalcone units, the quantum yield is a lot less among the four dendrimers.

The photoisomerization behavior of dendrimers **1**, **2**, **3**, and **4** were investigated by UV–vis spectrophotometry. The dendrimers (1×10^{-6} M in $CHCl_3$) were irradiated at 365 nm to induce

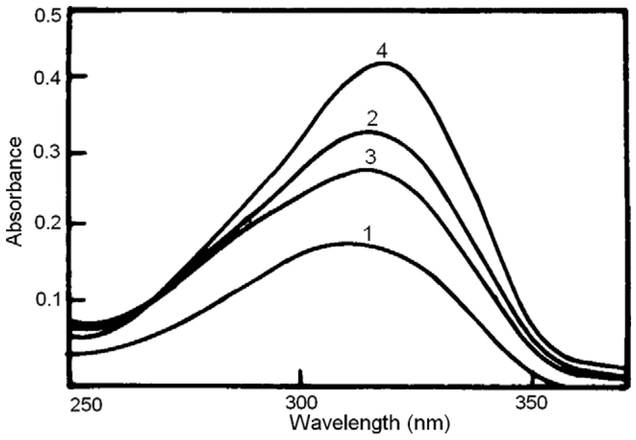


Figure 1. Absorption spectra of dendrimers **1**, **2**, **3**, and **4** in $CHCl_3$ (1×10^{-6} M).

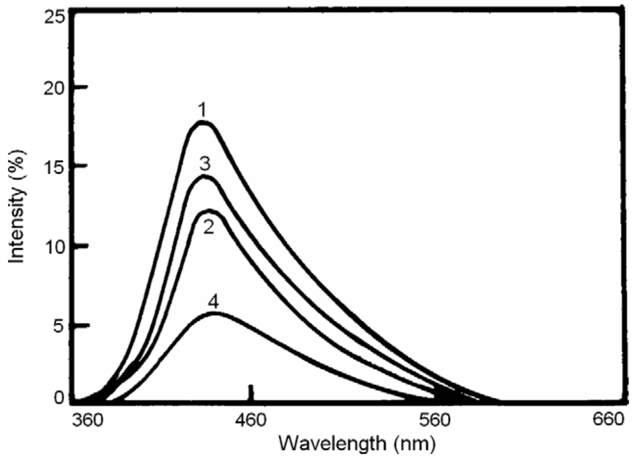


Figure 2. Emission spectra of dendrimers **1**, **2**, **3**, and **4** in $CHCl_3$ (1×10^{-6} M).

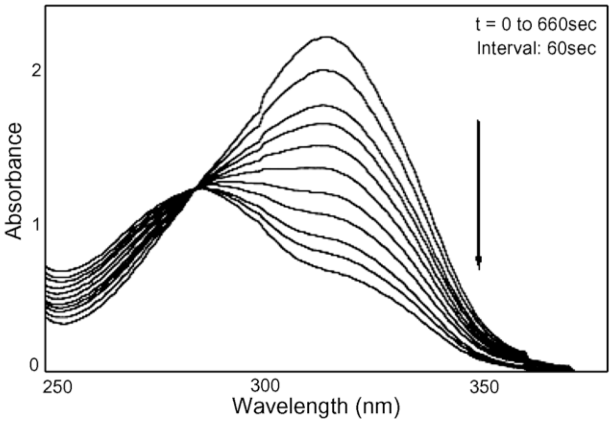


Figure 3. Photoisomerization of dendrimer **4** in $CHCl_3$ (1×10^{-5} M).

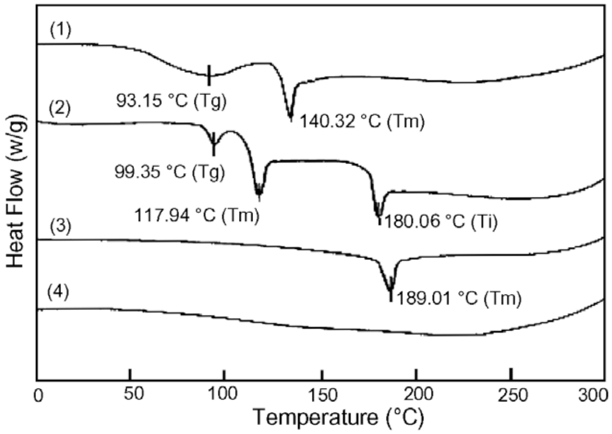


Figure 4. DSC curves of dendritic structures **1**, **2**, **3**, and **4**.

cis–trans isomerization. Figure 3 shows the UV–vis spectral changes of dendrimer **4** on UV irradiation. This dendrimer undergoes *cis–trans* isomerization as revealed by the decrease in the absorbance[28] and appearance of an isosbestic point at 285 nm. A photostationary state was attained within 660 s during which time most of the *trans* chalcone moieties were converted to the *cis* isomer. Similarly, dendritic architectures **1**, **2**, and **3** also underwent *cis–trans* isomerization.

The thermal behaviors of the dendritic structures **1**, **2**, **3**, and **4** were investigated through differential scanning calorimetry (DSC), and the results are shown in Figure 4. All the compounds were found to possess high thermal stability and decomposed above 300 °C. The glass transition temperatures (T_g) improved from 63 °C to 99 °C with an increase in the number of chalcone units in dendritic structures **1** and **2**. The T_g values could not be obtained clearly for dendrimers **3** and **4** due to the incorporation of more chalcone units in the dendritic structures. Among the dendrimers, only **2** showed an isotropic curve at 180.06 °C (Fig. 4), which indicates that the compound might exhibit liquid crystalline (LC) properties. Though dendrimer **4** has structural similarity with dendrimer **2**, an isotropic curve was not observed due to its decomposition at high temperature.

In summary, we have synthesized several chalcone-based dendritic structures and have studied their optical and thermal properties. The incorporation of increased numbers of chalcone units at the peripheries of the dendritic architectures had significant effects on improving the morphology. Syntheses of chalcone dendritic architectures with various substituents through click chemistry and their biological properties are currently under investigation.

Acknowledgments

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22. Dendron **8**: Yield 83%, 65%, mp 165 °C (dec); ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.18 (s, 4H); 6.86 (s, 2H); 7.16 (d, 4H, J = 8.7 Hz); 7.45 (m, 7H); 7.71 (d, 2H, J = 15.6); 7.87 (d, 4H, J = 3.6 Hz); 7.94 (d, 2H, J = 15.6); 8.17 (d, 4H, J = 8.4 Hz); 9.67 (s, 1H): ^{13}C NMR (75 MHz, DMSO-d_6): δ 69.3, 113.9, 114.8, 117.2, 122, 128.7, 128.8, 130.4, 130.6, 130.9, 134.8, 138.2, 143.1, 157.6, 162.3, 187.3; MS (EI, 70 eV): m/z 566 (M$^+$). Elemental Anal. Calcd for $C_{38}H_{30}O_5$: C, 80.55; H, 5.34. Found: C, 80.42; H, 5.21.
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24. *Dendrimer* **1**: Yield 95%; mp 142 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.50 (s, 9H); 5.23 (s, 6H); 7.14 (d, 6H, J = 8.4 Hz); 7.44 (m, 9H); 7.58 (d, 3H, J = 15.6 Hz); 7.67 (d, 6H, J = 3.9 Hz); 7.84 (d, 3H, J = 15.6 Hz); 8.11 (d, 6H, J = 8.1 Hz): ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 65.2, 114.5, 121.9, 128.4, 128.9, 130.4, 130.9, 131.4, 131.5, 135.1, 139.6, 144.1, 162.9, 188.7; MS (EI, 70 eV): m/z 828 (M$^+$). Elemental Anal. Calcd for $C_{57}H_{48}O_6$: C, 82.58; H, 5.84. Found: C, 82.70; H, 5.97.
25. *Dendrimer* **2**: Yield 73%; mp 125 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 9H); 5.05 (s, 18H); 6.96 (m, 18H); 7.05 (s, 3H); 7.30 (s, 18H); 7.44 (d, 6H, J = 15.6 Hz); 7.52 (s, 12H); 7.70 (d, 6H, J = 15.9 Hz); 7.94 (d, 12H, J = 7.8 Hz): ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 65.1, 69.8, 113.3, 114.7, 118.8, 121.8, 128.4, 128.9, 130.4, 130.8, 131.5, 131.6, 135.0, 138.5, 139.4, 144.1, 159.7, 162.4, 188.6; (FAB-MS): m/z 1854 (M$^+$). Elemental Anal. Calcd for $C_{126}H_{102}O_{15}$: C, 81.53; H, 5.54. Found: C, 81.44; H, 5.41.
26. *Dendrimer* **3**: Yield 83%; mp 185 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.34 (s, 12H); 6.97 (d, 12H, J = 8.7 Hz); 7.35–7.37 (m, 18H); 7.44 (d, 6H, J = 15.6 Hz); 7.54–7.57 (m, 12H); 7.73 (d, 6H, J = 15.6 Hz); 7.96 (d, 12H, J = 9.0 Hz): ^{13}C NMR (75 MHz, $CDCl_3$): δ 63.9, 114.4, 121.5, 128.4, 128.9, 130.4, 130.9, 132.0, 134.9, 137.8, 144.4, 161.8, 188.5; (FAB-MS): m/z 1494 (M$^+$). Elemental Anal. Calcd for $C_{102}H_{78}O_{12}$: C, 81.91; H, 5.26. Found: C, 81.75; H, 5.13.
27. *Dendrimer* **4**: Yield 69%; mp 210 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.86 (s, 24H); 5.24 (s, 12H); 6.81–6.88 (m, 36H); 6.98 (s, 6H); 7.27 (s, 36H); 7.37 (d, 12H, J = 15.6 Hz); 7.48 (s, 24H); 7.65 (d, 12H, J = 15.6 Hz); 7.86 (d, 24H, J = 8.4 Hz): ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.1, 69.6, 113.5, 114.5, 119.4, 121.6, 128.4, 128.9, 130.4, 130.8, 131.5, 135.0, 138.0, 138.6, 144.2, 159.0, 162.2, 188.4; (FAB-MS): m/z 3548 (M$^+$). Elemental Anal. Calcd for $C_{240}H_{186}O_{30}$: C, 81.20; H, 5.28. Found: C, 81.44; H, 5.43.
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