

potassium indigotetrasulfonate into the Zn-Al LDH were determined. For the indigo carmine, the molecular plane of the indigo carmine and its C=C axis lie nearly perpendicular to the hydroxide layers. However, the molecular plane of the potassium indigotetrasulfonate is oriented perpendicular to the hydroxide layers, while its C=C axis is arranged parallel to the hydroxide layers. Therefore, the guest species play an important role in the intercalation of guest species into the Zn-Al LDH.

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## References

- Whittingham, M. S.; Jacobson, A. J. *Intercalation Chemistry*; Academic Press: New York, 1982.
- Orgawa, M.; Kuroda, K. *Chem. Rev.* 1995, 95, 399.
- Reichle, W. T. *Chemtech.* 1986, 58.
- Constantino, V. R. L.; Pinnavaia, T. J. *Inorg. Chem.* 1995, 34, 883.
- Itaya, K.; Chang, H. C.; Uchida, I. *Inorg. Chem.* 1987, 26, 624.
- Cooper, S.; Dutta, P. K. *J. Phys. Chem.* 1990, 94, 114.
- Rhee, S. W.; Kang, M. J.; Moon, H. C. *J. Korean Chem. Soc.* 1995, 39, 627.
- Busetto, C.; Del Piero, G.; Manara, G.; Trifiro, F.; Vaccari, A. *J. Catal.* 1984, 85, 260.
- Cervilla, A.; Corma, A.; Fornes, V.; Llopis, E.; Palanca, P.; Rey, F.; Ribera, A. *J. Am. Chem. Soc.* 1994, 116, 1595.
- Serna, C. J.; White, J. L.; Hem, S. L. *J. Pharma. Sci.* 1978, 67, 324.
- Climent, M. J.; Corma, A.; Iborra, S.; Primo, J. *J. Catal.* 1995, 151, 60.
- Chibwe, K.; Jones, W. *J. Chem. Soc., Chem. Commun.* 1989, 926.
- Tagaya, H.; Sato, S.; Morioka, H.; Kadokawa, J.; Karasu, M.; Chiba, K. *Chem. Mater.* 1993, 5, 1431.
- Park, I. Y.; Kuroda, K.; Kato, C. *J. Chem. Soc. Dalton Trans.* 1990, 3071.
- Miyata, S. *Clays Clay Miner.* 1983, 31, 305.
- Miyata, S.; Okada, A. *Clays Clay Miner.* 1977, 25, 14.
- Weast, R. C. *Handbook of Chemistry and Physics*, 70th ed.; p D-190.

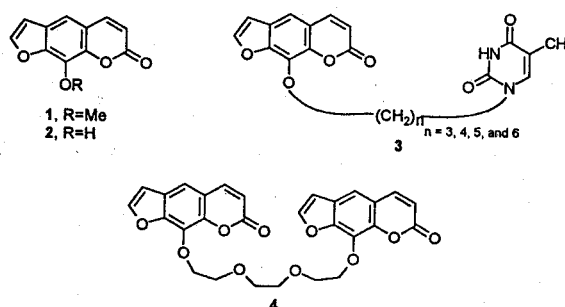
## Bispsoralen Derivatives Linked with a Polymethylene Bridge Containing a Hydroquinone Moiety

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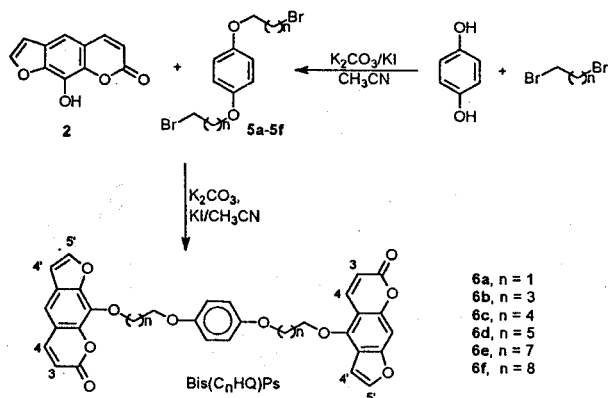
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Psoralens are widely used as dermal photosensitizing agents for the treatment of various skin diseases,<sup>1-4</sup> e.g., vitiligo, psoriasis, mycosis fungoides, chronic leukemia, and some infections connected with AIDS<sup>5</sup> and as chemical tools for the study of nucleic acid structure-function relationship.<sup>6,7</sup> A large number of studies on the mechanism of the photochemical reactions between psoralen and DNA bases *in vivo*<sup>8</sup> or with thymine derivatives<sup>9,10</sup> have been carried out. These studies involved intermolecular processes leading generally to a mixture of several photoproducts. Binding of psoralens to DNA is generally the consequence of two successive events: (a) intercalation of the psoralen between the base pairs of nucleic acids in the ground state;<sup>11,12</sup> (b) photo [2+2] conjugation of the complexed psoralen to pyrimidine bases of DNA between the pyrimidine 5,6 double bond and 3,4 and/or 4',5' double bond of the psoralen molecule.<sup>8,13</sup> The formation of the intercalated complex between psoralens and DNA is an important step which markedly affects the successive covalent photobinding to the macromolecule. In order to gain insight into these two processes in the absence of complicating factors associated with hydrogen bonding or the usual carbohydrate and phosphodiester linkages, Lhomme and Decout<sup>14</sup> prepared a series of model compounds **3** and showed that the polymethylene bridges allow intramolecular ring-ring stacking between the two aromatic units with possible superposition of the double bonds. Castellan *et al.*<sup>15</sup> also investigated the interactions and the photoreactions of synthetic derivatives of psoralen containing the psoralen and the thymine rings, the two psoralen rings (**4**), or the two thymine rings. The reactivity of the bispsoralen **4** were reported to be sensitive to the presence of cations because the cation added made the conformation of the polyoxyethylene chain folded, increasing the intramolecular interaction between two psora-



**Figure 1.** Chemical Structures of 8-MOP (**1**), 8-hydroxypsoralen (**2**) and psoralen analogues (**3**, **4**).



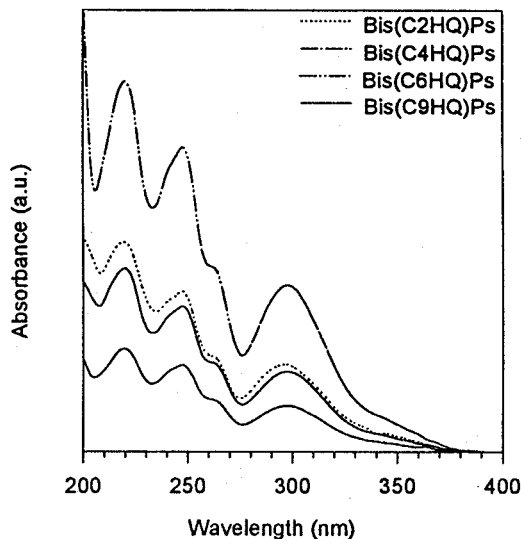
**Scheme 1.** Syntheses of bispsoralen derivatives (6a-6f).

len chromophores.

It seemed to be of interest to perform further studies with new bispsoralen analogs whose structures allow cross-linking of DNA and we devised synthetic models **6** in which the psoralens are linked by a polymethylene chain containing a hydroquinone moiety. The third aromatic unit, hydroquinone moiety, reduces intramolecular interactions due to the inflexibility and the bulkiness of hydroquinone. It is, therefore, expected that the psoralen derivatives **6** will prefer an interstrand cross-linking between two DNA strands to an intramolecular cross-linking in a DNA strand. The model compounds **6** are expected to be good chemical probes for the study of photobinding to DNA such as *plasmid* DNA or *calf thymus* DNA and to be a chemical drug to prevent the replication of DNA due to four binding sites (3,4- and 4',5'-double bonds for each psoralen chromophore). A series of such molecules were synthesized as shown in Scheme 1. Alkylation of hydroquinone with  $\alpha,\omega$ -dibromoalkanes in refluxing acetonitrile in the presence of  $\text{K}_2\text{CO}_3$  afforded the corresponding bis( $\omega$ -bromoalkoxy)-benzene (**5a-5f**). Reaction of the links, bis(bromo-alkoxy)benzene **5a-5f**, with 8-hydroxy-psoralen (**2**) under the same reaction conditions furnished the bispsoralen **6a-6f** in 25%-70% yields. All new compounds were confirmed by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, Mass, and UV spectra. All spectra were in accordance with the structures indicated. IR spectra of all compounds are characterized by a strong sharp band at  $1717\text{-}1728\text{ cm}^{-1}$ . In  $^1\text{H}$  NMR spectra, signals of C(3)-H, C(4)-H, C(4')-H, and C(5')-H protons in **6a-6f** appear as doublets at 6.76-6.78 ppm ( $J=2.2$  Hz), 7.62-7.65 ppm ( $J=2.2$  Hz), 6.29-6.33 ppm ( $J=9.6$  Hz), and 7.69-7.73 ppm ( $J=9.6$  Hz), respectively. The UV absorption spectra of bispsoralen (**6a**, **6b**, **6d**, and **6f**) show nearly the same pattern as other psoralen derivatives in the range of 200 nm-400 nm at various concentrations, showing maximum intensities at 297 nm, 248 nm, 219 nm, a small maximum intensity at 262 nm, and a broad shoulder in the long UVA region from 330 nm to 380 nm in methanol (Figure 2).

In conclusion, new bispsoralen derivatives which have polymethylene-hydroquinone chains of varying length ( $\text{CH}_2$ ) $_n$  are prepared as potential intercalating drugs and molecular probes for the photobinding to DNA.

## Experimental Section



**Figure 2.** UV absorption spectra of Bis(C $_n$ HQ)Ps; ( $n=2,4,6$ , and 9) in MeOH.

**General Procedure.** All reactions were carried out under dry nitrogen in oven-dried glassware. Reagent grade acetonitrile ( $\text{CH}_3\text{CN}$ ) was distilled under nitrogen from calciumhydride. Bulk grade hexane was distilled prior to use. Merck precoated silica gel plates (Art. 5554) with fluorescent indicator were used as analytical TLC. Gravity column chromatography and flash chromatography was carried out on silica gel (230-400 mesh from Merck).

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-200 MHz spectrometer. Proton chemical shifts ( $\delta$ ) are reported in ppm downfield from tetramethylsilane (TMS), and  $^{13}\text{C}$  resonances were recorded using the 77.0 ppm  $\text{CDCl}_3$  resonance of the solvent as an internal reference and reported in ppm downfield from TMS. Infrared spectra were recorded on a Bomem MB-100 Series FTIR spectrophotometer. Mass spectra were determined at 70 eV with a Hewlett-Packard 5985A GC/MS spectrometer. Melting points were determined in capillary tubes on a Thomas Hoover capillary melting point apparatus.

**1,4-Bis(6-bromo-hexyloxy)benzene (5d). General procedure.** 1,6-Dibromohexane (1.46 g, 5.99 mmol) was refluxed in  $\text{CH}_3\text{CN}$  (20 mL) with hydroquinone (300 mg, 2.73 mmol),  $\text{K}_2\text{CO}_3$  (1.90 g, 13.6 mmol), and KI (45 mg, 0.27 mmol) for 12h. The mixture was filtered after cooling, and the filter cake was washed with ethylacetate. Following removal of the solvent *in vacuo*, the residue was crystallized from ethylacetate and hexane (10 : 1) to yield 420 mg (36%) of the compound **5d** as a white solid: mp 88-90 °C;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  6.79 (4H, t), 3.88 (4H, t), 3.40 (4H, t), 1.90-1.71 (8H, m), and 1.55-1.43 (8H, m);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  153.11 (C), 115.36 (CH), 68.32 ( $\text{OCH}_2$ ), 33.80 ( $\text{CH}_2$ ), 32.66 ( $\text{CH}_2$ ), 29.17 ( $\text{CH}_2$ ), 27.90 ( $\text{CH}_2$ ), and 25.27 ( $\text{CH}_2$ ); IR (NaCl)  $\text{cm}^{-1}$  2937, 2862, 1510, 1476, 1461, 1245, 1236, 1113, 1028, 824, 771, and 729; Mass ( $m/e$ , %) 55 (76.9), 83 (30.3), 109 (11.6), 110 (100), 111 (14.5), 434 (7.2), 436 (19.9), and 438 (7.7).

**Preparation of 1,4-Bis(2-bromoethoxy)benzene (5a).** Reaction of 1,2-dibromoethane (2.18 g, 11.6 mmol), hyd-

roquinone (581 mg, 5.27 mg),  $K_2CO_3$  (3.64 g, 26.4 mmol), and KI (44.0 mg, 0.05 mmol) was carried out as described for the preparation of **5d** to obtain 280 mg (16%) of **5a**. mp 90-92 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  6.84 (4H, s), 4.23 (4H, t), and 3.59 (4H, t);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ) 152.77 (C), 116.04 (CH), 68.66 (OCH<sub>3</sub>), and 29.24 (CH<sub>2</sub>).

**Preparation of 1,4-Bis(4-bromobutoxy)benzene (5b).** Reaction of 1,4-dibromobutane (949 mg, 4.40 mmol), hydroquinone (220 mg, 2.0 mmol),  $K_2CO_3$  (1.38 g, 10.0 mmol), and KI (20 mg, 0.02 mmol) was carried out as described for the preparation of **5d** to obtain 233 mg (31%) of **5b**. mp 83-85 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  6.79 (4H, s), 3.91 (4H, t), 3.46 (4H, t), 2.08-1.97 (4H, m), and 1.95-1.85 (4H, m);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  153.03 (C), 115.36 (CH), 67.40 (OCH<sub>2</sub>), 33.49 (CH<sub>2</sub>), 29.46 (CH<sub>2</sub>), and 27.95 (CH<sub>2</sub>).

**Preparation of 1,4-Bis(5-bromopentyl)benzene (5c).** Reaction of 1,5-dibromopentane (1.39 g, 6.0 mmol), hydroquinone (300 mg, 2.73 mmol),  $K_2CO_3$  (1.88 mg, 13.6 mmol), and KI (45.0 mg, 0.27 mmol) was carried out as described for the preparation of **5d** to obtain 484 mg (44%) of **5c**. mp 76-78 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  6.79 (4H, s), 3.89 (4H, t), 3.41 (4H, t), 1.98-1.70 (8H, m), and 1.66-1.54 (4H, m);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  153.07 (C), 115.36 (CH), 68.15 (OCH<sub>2</sub>), 33.61 (CH<sub>2</sub>), 32.47 (CH<sub>2</sub>), 28.50 (CH<sub>2</sub>), and 24.81 (CH<sub>2</sub>); IR (NaCl)  $cm^{-1}$  3050, 2943, 2866, 1509, 1469, 1227, 1114, 1042, 1000, 824, and 736; Mass (m/e, %) 69 (94.4), 81 (8.0), 109 (15.5), 110 (88.4), 111 (7.9), 148 (22.6), 149 (23.3), 150 (8.6), 151 (22.4), 406 (4.4), 408 (7.3), and 410 (5.1).

**Preparation of 1,4-Bis(8-octyloxy)benzene (5e).** Reaction of 1,8-dibromooctane (1.63 g, 6.0 mmol), hydroquinone (300 mg, 2.73 mmol),  $K_2CO_3$  (1.90 g, 13.6 mmol), and KI (45.0 mg, 0.27 mmol) was carried out as described for the preparation of **5d** to obtain 465 mg (35%) of **5e**. mp 75-77 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  6.79 (4H, s), 3.88 (4H, t), 3.40 (4H, t), 1.90-1.71 (8H, m), and 1.55-1.43 (8H, m);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  153.12 (C), 115.33 (CH), 68.50 (OCH<sub>2</sub>), 33.97 (CH<sub>2</sub>), 32.75 (CH<sub>2</sub>), 29.30 (CH<sub>2</sub>), 29.10 (CH<sub>2</sub>), 28.65 (CH<sub>2</sub>), 28.06 (CH<sub>2</sub>), and 25.93 (CH<sub>2</sub>); IR (NaCl)  $cm^{-1}$  2933, 2857, 1511, 1470, 1288, 1236, 1113, 1027, 907, 825, and 731; Mass (m/e, %) 55 (42.0), 69 (32.1), 81 (25.1), 109 (9.5), 110 (100), 111 (15.4), 490 (8.9), 492 (15.2), and 494 (7.9).

**Preparation of 1,4-Bis(9-nonyloxy)benzene (5f).** Reaction of 1,9-dibromononane (1.71 g, 6.0 mmol), hydroquinone (300 mg, 2.73 mmol),  $K_2CO_3$  (1.90 g, 13.6 mmol), and KI (45.0 mg, 0.27 mmol) was carried out as described for the preparation of **5d** to obtain 550 mg (39%) of **5f**. mp 70-72 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  6.79 (4H, s), 3.87 (4H, t), 3.38 (4H, t), 1.86-1.66 (8H, m), and 1.40-1.31 (20H, m);  $^{13}C$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  153.12 (C), 115.31 (CH), 68.52 (OCH<sub>2</sub>), 33.99 (CH<sub>2</sub>), 32.76 (CH<sub>2</sub>), 29.31 (CH<sub>2</sub>), 29.31 (CH<sub>2</sub>), 29.23 (CH<sub>2</sub>), 28.64 (CH<sub>2</sub>), 28.09 (CH<sub>2</sub>), and 25.97 (CH<sub>2</sub>); IR (NaCl)  $cm^{-1}$  2928, 2851, 1509, 1463, 1227, 1115, 1043, 1022, 828, 772, and 726; Mass (m/e, %) 55 (73.0), 69 (36.1), 83 (12.2), 109 (9.6), 110 (100), 111 (23.1), 518 (12.4), 520 (19.2), and 522 (12.7).

#### Synthesis of Bis(C6HQ)Ps (6d). General Procedure.

A mixture of 1,4-bis(2-bromohexyloxy)benzene (218 mg, 0.50 mmol), 8-hydroxy-psoralen (222 mg, 1.10 mmol),  $K_2CO_3$  (346 mg, 2.50 mmol), and KI (16 mg, 0.10 mmol) in 5 mL of  $CH_3CN$  was refluxed at 95-105 °C under a nitrogen atmos-

phere for 12 h. After filtration,  $CH_3CN$  was evaporated under reduced pressure. Purification of the residue by column chromatography on silica gel (eluent: 30% ethylacetate in hexane) gave the pure compound **6d** as a white solid (150 mg, 44%): mp 89-91 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  7.70 (2H, d,  $J=9.6$  Hz), 7.62 (2H, d,  $J=2.2$  Hz), 7.29 (2H, s), 6.77 (4H, s), 6.76 (2H, d,  $J=2.2$  Hz), 6.30 (2H, d,  $J=9.6$  Hz), 4.44 (4H, t), 3.87 (4H, t), 1.88-1.72 (8H, m), and 1.59-1.49 (8H, m);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  160.42 (CO), 153.02 (C), 148.05, 146.50, 144.28, 143.30, 131.85, 125.85, 116.37, 115.25, 114.49, 112.94, 106.63, 73.82 (OCH<sub>2</sub>), 68.32 (OCH<sub>2</sub>), 29.90 (CH<sub>2</sub>), 29.18 (CH<sub>2</sub>), 25.69 (CH<sub>2</sub>), and 25.42 (CH<sub>2</sub>); IR (NaCl)  $cm^{-1}$  3146, 3118, 3063, 2937, 2863, 1727, 1622, 1586, 1507, 1468, 1440, 1398, 1331, 1292, 1223, 1178, 1149, 1097, 1029, 870, 824, and 749; UV (MeOH)  $\lambda_{max}$  297.4, 248.1, and 219.2 nm.

**Preparation of Bis(C2HQ)Ps (6a).** Reaction of **5a** (70 mg, 0.22 mmol) with 8-hydroxy-psoralen (96 mg, 0.48 mmol) in the presence of  $K_2CO_3$  (149 mg, 1.08 mmol) and KI (3.6 mg, 0.02 mmol) as described for the preparation of **6d** yielded 30 mg (25%) of **6a**. mp 164-167 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  7.73 (2H, d,  $J=9.6$  Hz), 7.63 (2H, d,  $J=2.2$  Hz), 7.34 (2H, s), 6.78 (2H, d,  $J=2.2$  Hz), 6.75 (4H, s), 6.32 (2H, d,  $J=9.6$  Hz), 4.77 (4H, t), and 4.31 (4H, t);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  160.32 (CO), 152.91 (C), 148.04, 146.70, 144.29, 143.29, 131.65, 125.91, 116.42, 115.66 (CH), 114.62, 113.44, 106.67, 71.96 (CH<sub>2</sub>), and 67.97 (CH<sub>2</sub>); IR (NaCl)  $cm^{-1}$  3142, 3118, 3063, 2931, 2875, 1725, 1623, 1587, 1506, 1445, 1401, 1330, 1219, 1151, 1100, 1072, 1027, 988, 872, 823, and 752; UV (MeOH)  $\lambda_{max}$  296.0, 248.3, and 219.5 nm.

**Preparation of Bis(C4HQ)Ps (6b).** Reaction of **5b** (202 mg, 0.53 mmol) with 8-hydroxy-psoralen (236 mg, 1.17 mmol),  $K_2CO_3$  (367 mg, 2.66 mmol) and KI (10 mg, 0.05 mmol) as described for the preparation of **6d** yielded 142 mg (43%) of **6b**. mp 153-155 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  7.71 (2H, d,  $J=9.6$  Hz), 7.62 (2H, d,  $J=2.2$  Hz), 7.30 (2H, s), 6.77 (4H, t), 6.76 (2H, d,  $J=2.2$  Hz), 4.50 (4H, t), 3.98 (4H, t), and 2.03-1.98 (8H, m);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  160.42 (CO), 152.98 (C), 148.00, 146.53, 144.29, 143.28, 131.75, 125.89, 116.38, 115.27 (CH), 114.52, 113.01, 106.65, 73.49 (OCH<sub>2</sub>), 67.92 (OCH<sub>2</sub>), 26.72 (CH<sub>2</sub>), and 25.74 (CH<sub>2</sub>); IR (NaCl)  $cm^{-1}$  3152, 3112, 3084, 2954, 2873, 1717, 1626, 1587, 1504, 1467, 1439, 1398, 1331, 1293, 1214, 1196, 1181, 1150, 1086, 1043, 1030, 992, 966, 885, 872, 830, 759, and 744; UV (MeOH)  $\lambda_{max}$  297.1, 248.4, and 217.6 nm.

**Preparation of Bis(C5HQ)Ps (6c).** Reaction of **5c** (204 mg, 0.50 mmol) with 8-hydroxy-psoralen (222 mg, 1.10 mmol),  $K_2CO_3$  (346 mg, 2.50 mmol) and KI (16 mg, 0.1 mmol) as described for the preparation of **6d** yielded 144 mg (44%) of oily **6c**.  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  7.69 (2H, d,  $J=9.6$  Hz), 7.61 (2H, d,  $J=2.2$  Hz), 7.27 (2H, s), 6.76 (4H, s), 6.75 (2H, d,  $J=2.2$  Hz), 6.28 (2H, d,  $J=9.6$  Hz), 4.44 (4H, t), 3.88 (4H, t), and 1.91-1.67 (12H, m);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  160.36 (CO), 152.92 (C), 147.93, 146.46, 144.26, 143.19, 131.71, 125.81, 116.29, 115.19 (CH), 114.38, 112.96, 106.60, 73.64 (OCH<sub>2</sub>), 68.18 (OCH<sub>2</sub>), 29.66 (CH<sub>2</sub>), 28.96 (CH<sub>2</sub>), 28.89 (CH<sub>2</sub>), and 22.21 (CH<sub>2</sub>); IR (NaCl)  $cm^{-1}$  3147, 3117, 3063, 2941, 2868, 1727, 1622, 1586, 1507, 1468, 1440, 1399, 1331, 1292, 1223, 1179, 1149, 1097, 1028, 990, 870, 824, and 748; UV (MeOH)  $\lambda_{max}$  296.9, 247.9, and 218.3 nm.

**Preparation of Bis(C8HQ)Ps (6e).** Reaction of **5e**

(246 mg, 0.50 mmol) with 8-hydroxypsoralen (222 mg, 1.10 mmol),  $K_2CO_3$  (346 mg, 2.50 mmol) and KI (16 mg, 0.10 mmol) as described for the preparation of **6d** yielded 257 mg (70%) of **6e**. mp 81-82 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  7.72 (2H, d,  $J=9.6$  Hz), 7.64 (2H, d,  $J=2.2$  Hz), 7.31 (2H, s), 6.78 (4H, s), 6.77 (2H, d,  $J=2.2$  Hz), 6.32 (2H, d,  $J=9.6$  Hz), 4.45 (4H, t), 3.86 (4H, t), 1.87-1.65 (8H, m), and 1.55-1.37 (16H, m);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  160.51 (CO), 153.10 (C), 148.16 (C), 146.55, 144.32, 143.39, 132.01, 125.91, 116.46, 115.31 (CH), 114.63, 112.90, 106.67, 74.04 ( $OCH_2$ ), 68.54 ( $OCH_2$ ), 30.01 ( $CH_2$ ), 29.30 ( $CH_2$ ), 29.24 ( $CH_2$ ), 29.20 ( $CH_2$ ), 25.92 ( $CH_2$ ), and 25.60 ( $CH_2$ ); IR (NaCl)  $cm^{-1}$  3140, 3118, 3060, 2932, 2856, 1728, 1622, 1586, 1507, 1467, 1440, 1400, 1331, 1292, 1224, 1148, 1098, 1028, 870, 823, and 753; UV (MeOH)  $\lambda_{max}$  297.1, 248.4, and 220.7 nm.

**Preparation of Bis(C9HQ)Ps (6f).** Reaction of **5f** (260 mg, 0.50 mmol) with 8-hydroxypsoralen (222 mg, 1.10 mmol) in the presence of  $K_2CO_3$  (346 mg, 2.50 mmol) and KI (16 mg, 0.10 mmol) as described for the preparation of **6d** yielded 237 mg (62%) of **6f**. mp 75-77 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  7.72 (2H, d,  $J=9.6$  Hz), 7.64 (2H, d,  $J=2.2$  Hz), 7.30 (2H, s), 6.78 (4H, s), 6.77 (2H, d,  $J=2.2$  Hz), 6.32 (2H, d,  $J=9.6$  Hz), 4.44 (4H, t), 3.85 (4H, t), 1.86-1.64 (8H, m), and 1.54-1.33 (20H, m);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  160.50 (CO), 153.07 (C), 148.13 (C), 146.52, 144.32, 143.36, 131.99, 125.89, 116.42, 115.28 (CH), 114.59, 112.89, 106.66, 74.04 ( $OCH_2$ ), 68.52 ( $OCH_2$ ), 30.01 ( $CH_2$ ), 29.38 ( $CH_2$ ), 29.30 ( $CH_2$ ), 29.24 ( $CH_2$ ), 29.20 ( $CH_2$ ), 25.95 ( $CH_2$ ), and 25.62 ( $CH_2$ ); IR (NaCl)  $cm^{-1}$  3138, 3118, 3055, 2929, 2855, 1728, 1622, 1586, 1507, 1467, 1440, 1399, 1331, 1292, 1224, 1179, 1148, 1098, 1029, 990, 871, 823, and 753; UV (MeOH)  $\lambda_{max}$  297.3, 248.3, and 220.6 nm.

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## References

1. Scott, B. R.; Pathak, M. A.; Mohn, G. R. *Mutat. Res.* **1976**, *39*, 29.
2. (a) Parrish, J. A.; Stern, P. S.; Pathak, M. A.; Fitzpatrick, T. B. *The Science of Photomedicine*; Plenum Press: New York, **1982**, 595-624. (b) Parrish, J. A.; Fitzpatrick, T. B.; Tanenbaum, L.; Pathak, M. A. *New Engl. J. Med.* **1974**, *291*, 1207.
3. Edelson, R.; Berger, C.; Gasparro, F.; Jegasothy, B.; Heald, P.; Wintroub, B.; Vonderheid, E.; Knobler, R.; Wolff, K.; Plewig, G.; Mckiernan, G.; Christensen, I.; Oster, M.; Honigsmann, H.; Wilford, H.; Kokoschka, E.; Rehle, T.; Perez, M.; Stingl, G.; Laroche, L. *New Engl. J. Med.* **1987**, *316*, 297.
4. Knobler, R. M.; Honigsmann, H.; Edelson, R. L. Psoralen Phototherapies. In *Psoralen DNA Photobiology* (Edited by Gasparro, F. T.), 1988; Vol. II. 117-134. CRC Press, Boca Raton, Florida.
5. Gorin, J.; Lessana-Leibowitch, M.; Fortier, P.; Leibowitch, J.; Escande, J.-P. *J. Amer. Acad. Dermatol.* **1989**, *20*, 511.
6. (a) Cimino, G. P.; Gamper, H. B.; Isaacs, S. T.; Hearst, J. E. *Ann. Rev. Biochem.* **1985**, *54*, 1151. (b) Hearst, J. E. *Ann. Rev. Biophys. Bioeng.* **1985**, *10*, 69.
7. (a) Shen, C.-K. J.; Hsieh, T.-S.; Wang, J. C.; Hearst, J. E. *J. Mol. Biol.* **1977**, *116*, 661. (b) Shen, C.-K. J.; Hearst, J. E. *Proc. Natl. Acad. Sci. USA*, **1976**, *73*, 2649.
8. (a) Bordin, F.; Marzano, C.; Gatto, C.; Carassare, F.; Rodighiero, P.; Baccichetti, F. *J. Photochem. Photobiol. B: Biol.* **1994**, *26*, 197. (b) Chen, X.; Kagan, J.; Dall'Acqua, F.; Averbek, D.; Bisagni, E. *J. Photochem. Photobiol. B: Biol.* **1994**, *22*, 51. (c) Song, P.-S.; Tapley, Jr., K. J. *Photochem. Photobiol.* **1979**, *29*, 1177. (d) Dall'Acqua, F.; Marciani Magno, S.; Leonard, N. J. *Photochem. Photobiol.* **1979**, *29*, 489. (e) Fujita, H.; Sano, M.; Suzuki, K. *Photochem. Photobiol.* **1979**, *29*, 71.
9. Musajo, L.; Bordin, F.; Caporale, G.; Marciani, S.; Rigatti, G. *Photochem. Photobiol.* **1967**, *6*, 711.
10. (a) Rodighiero, G.; Dall'Acqua, F. *Photochem. Photobiol.* **1976**, *24*, 647. (b) Parsons, B. J. *Photochem. Photobiol.* **1980**, *32*, 813.
11. Dall'Acqua, F.; Terbojevich, M.; Marciani Magno, S.; Veldaldi, D.; Recher, M. *Chem. Biol. Interact.* **1978**, *21*, 103.
12. Ronto, G.; Toth, K.; Gaspar, S.; Csik, G. J. *Photochem. Photobiol., B: Biol.* **1992**, *12*, 9.
13. Hearst, J. E.; Isaacs, S. T.; Kanne, D.; Rapoport, H.; Straub, K. Q. *Rev. Biophys.* **1984**, *17*, 1.
14. (a) Decout, J. L.; Huart, G.; Lhomme, J. *Photochem. Photobiol.* **1988**, *48*, 583. (b) Decout, J. L.; Lhomme, J. *Photochem. Photobiol.* **1983**, *37*, 155. (c) Decout, J. L.; Lhomme, J. *Tetrahedron Lett.* **1981**, *22*, 1247.
15. Castellani, A.; Desvergne, J. P. *Photochem. Photobiol.* **1981**, *34*, 183.

## Efficient Synthesis of Tetrathiol and Octathia-carceplex. First Attempt to Estimate Guest's Peak by $^1H$ NMR Data Comparison

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Cram and co-workers, container hosts are synthetic molecules having an enforced cavity capable of embracing guest ions or molecules.<sup>1</sup> Most of them are based on the derivatives of resorcarenes formed by acid-catalyzed cyclotetramerization between resorcinol (or its derivatives) and various aldehydes. The prototype carcerands **1** (tetrathiacarcarands,  $D_{4h}$  point group) were made by shell-closing reactions of compounds **7** and **8** ( $R=CH_3$  or  $(CH_2)_4CH_3$ ) obtained from tetrabromide **6** and revealed many unprecedented properties