

environment, resulting in readily processable materials, will enhance their potential for practical applications. To be presented in this communication are novel chemical systems and their glass-forming ability as determined by the ability to vitrify on cooling from melt and the stability against recrystallization on heating from below glass-transition temperature up to crystalline melting point. The tendency for excimer formation as determined by the inherent nature of the chromophore and the stereochemistry as imposed by the central core will also be elucidated with fluorescence characteristics in dilute solutions.

## II. Experimental Section

**Reagents and Chemicals.** All solvents and reagents were used as received from the Aldrich Chemical Company or VWR Scientific with the following exceptions: Tetrahydrofuran (99%) was dried by refluxing over sodium in the presence of benzophenone until blue and then distilled. Prior to their use, 1-pyrenylmethanol and *N*-ethylcarbazole were recrystallized from methanol and *n*-hexane, respectively. The synthesis of 1,3,5,7-adamantanetetracarboxylic acid chloride was accomplished by photochemical chlorocarbonylation of 1,3-adamantanedicarboxylic acid in an excess of oxalyl chloride as reported previously.<sup>14</sup>

**Material Synthesis.** *Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid and trans-1,3,5-cyclohexanetricarboxylic acids:* Hydrolysis of bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride in boiling water followed by recrystallization from water yielded bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid. Proton NMR (in DMSO-*d*<sub>6</sub>),  $\delta$  11.92 (s, 4H, carboxylic acid),  $\delta$  6.06 (d, 2H, alkene),  $\delta$  2.99 [s, 6H, overlap of bridgehead (2H) and methine (4H) signals]. A procedure reported by Steiz<sup>15</sup> was followed to convert commercially available *cis*-1,3,5-cyclohexanetricarboxylic acid into a *trans* isomer with a 1-axial 2-equatorial configuration.

*3-(N-Carbazolyl)propanol:* 3-bromo-1-propanol was protected with the tetrahydropyranyl group following previously reported procedures.<sup>16</sup> Carbazole was reacted with the THP-protected 3-bromo-1-propanol followed immediately by cleavage of the protecting group to yield the precursor alcohol. The procedure is as follows: carbazole (4.99 g, 29.8 mmol), THP-protected 3-bromo-1-propanol (7.38 g, 33.1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (19.5 g, 59.8 mmol), and KI (0.5 g, 3 mmol) were stirred with 50 mL of anhydrous DMF under dry nitrogen. The slurry was heated to 85–90 °C for 12 h. The reaction mixture was shaken with 100 mL of diethyl ether and 100 mL of water, and the layers were separated. The organic layer was washed with water (100 mL  $\times$  3) and evaporated to dryness. Ethanol (50 mL) and pyridinium *p*-toluenesulfonate (2 g, 8 mmol) were added to the solid residue. A temperature of about 60 °C was maintained for 15 h followed by workup with diethyl ether and water. The crude product was purified by flash chromatography on silica gel using methylene chloride/acetone (40:1) as the eluent, yielding 3-(*N*-carbazolyl)propanol (2.99 g, 44%). Proton NMR (in CDCl<sub>3</sub>):  $\delta$  7.25–8.12 [m, 8H, aromatic], 4.50 [t, 2H, CH<sub>2</sub>CH<sub>2</sub>N], 3.64 [t, 2H, HOCH<sub>2</sub>CH<sub>2</sub>], 2.15 [m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>], and 1.48 [s, 1H, OH].

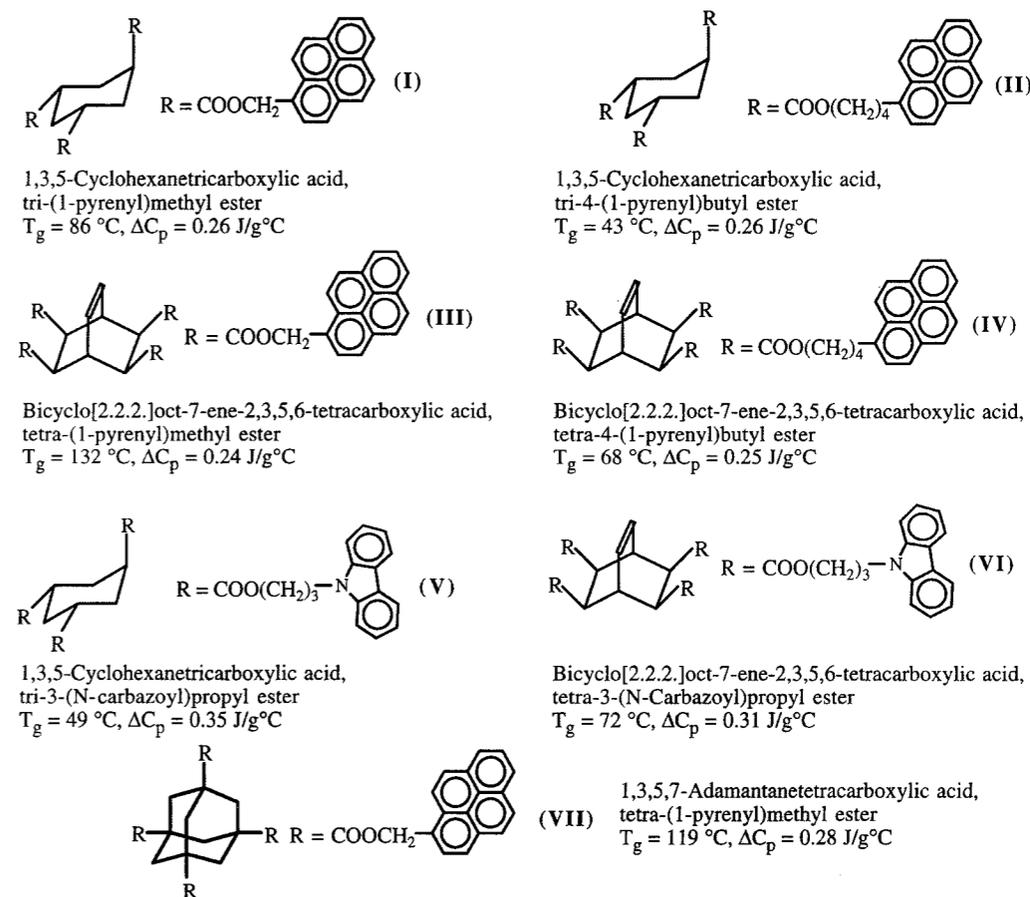
*Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid, tetraakis[4-(1-pyrenyl)butyl] ester:* All seven ester products were made by reacting a precursor alcohol with *trans*-1,3,5-cyclohexanetricarboxylic acid, *exo*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid, and 1,3,5,7-adamantanetetracarboxylic acid chloride following the general procedures as accomplished previously.<sup>7–9</sup> The procedures involved in synthesis and purification are illustrated as follows. Under a dry nitrogen atmosphere, 4-(1-pyrenyl)butanol (0.545 g, 1.986 mmol), *exo*-bicyclo-

[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid (0.141 g, 0.496 mmol), and triphenylphosphine (0.696 g, 2.66 mmol) were dissolved in dry tetrahydrofuran (8 mL) and dry DMF (4 mL). Diethylazodicarboxylate (0.44 mL, 2.8 mmol) was then added dropwise over 15 min. About 2 h later, the reaction mixture was shaken with diethyl ether (100 mL) and water (100 mL). The organic layer was dried over anhydrous MgSO<sub>4</sub> before evaporating the solvent to dryness. The crude product was obtained by flash chromatography on silica gel using methylene chloride/acetone (40:1) as the eluent. It was further purified by a gradient elution with methylene chloride/hexane (3:1) gradually changed to methylene chloride/acetone (5:1) as the eluent to obtain the pure product (0.24 g, 37%). Proton NMR (in CDCl<sub>3</sub>)  $\delta$  8.14–7.72 [m, 36 H, aromatic], 6.37 [m, 2 H, HC=CH], 3.98 [m, 4 H, COOCH<sub>2</sub>H<sub>B</sub>CH<sub>2</sub>], 3.87 [m, 4 H, COOCH<sub>A</sub>H<sub>B</sub>CH<sub>2</sub>], 3.26 [s, 2 H, bridgehead], 3.18 [t, 8 H, COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>], 2.90 [s, 4 H, CHCOO], 1.70 [m, 8 H, COOCH<sub>A</sub>H<sub>B</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>], 1.62 [m, 8 H, COOCH<sub>A</sub>H<sub>B</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>].

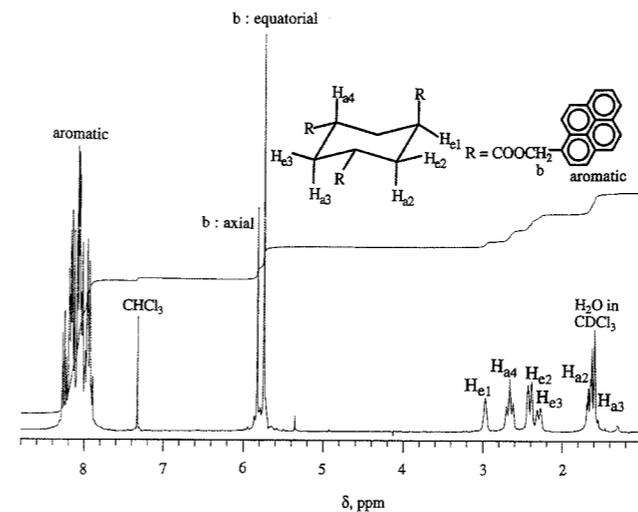
**Characterization Techniques.** A Hitachi high-performance liquid chromatography (HPLC) system comprising an L-2000 metering pump and an L-4200 UV-vis absorbance detector equipped with an LiChrosorb column (RP-18, 10  $\mu$ m) was employed to determine the number of components and purity of the intermediates and products. The purity levels of all final products were found to be better than 99% based on HPLC analysis. Chemical structures were elucidated with elemental analysis (performed by Oneida Research Services, Inc. in Whitesboro, NY), FTIR (Nicolet 20 SX), and proton NMR (QE-300, GE) spectroscopic techniques. A Perkin-Elmer MPF-66 fluorescence spectrophotometer with a xenon lamp was used to acquire emission spectra in dilute solutions at room temperature. Thermal transition temperatures were determined by differential scanning calorimetry (DSC, Perkin-Elmer DSC-7) with a continuous nitrogen purge at 20 mL/min. A heating rate of 20 °C/min in DSC experiments was normally employed to gather a thermogram unless noted otherwise.

## III. Results and Discussion

Pyrene- and carbazole-containing cyclohexane, bicyclooctene, and adamantane systems synthesized for the present study are as depicted in Figure 1. The chemical structures are consistent with the elemental analysis and proton NMR spectral data compiled in ref 17. To facilitate our interpretation of NMR spectra in what follows, the spectrum of 1-pyrenylmethanol in CDCl<sub>3</sub> was gathered. The singlet at  $\delta$  5.39 is attributed to the methylene protons, thus precluding the possibility of long-range coupling with the ortho aromatic proton. The 1-axial 2-equatorial configuration on the cyclohexane ring was confirmed by comparing the NMR spectral region from  $\delta$  1.6 to 3.0, as illustrated in Figure 2 for compound I, characteristic of protons on the cyclohexane ring as elucidated previously.<sup>18</sup> The two singlets at  $\delta$  5.71 and 5.79 with integrations in the ratio 2:1 are clearly associated with the methylene protons between the pyrenyl and carboxylate groups in the equatorial and axial positions, respectively. In view of the fact that the more viscous DMSO was needed as a solvent for gathering the proton NMR spectrum of compound III, it was decided that the spectrum should also be taken of compound I in DMSO-*d*<sub>6</sub>. Again the three methylene groups appear as two singlets at  $\delta$  5.70 and 5.74 with integrations in the ratio 2–1 corresponding to equatorial and axial positions, indicating free rotation of pyrenyl



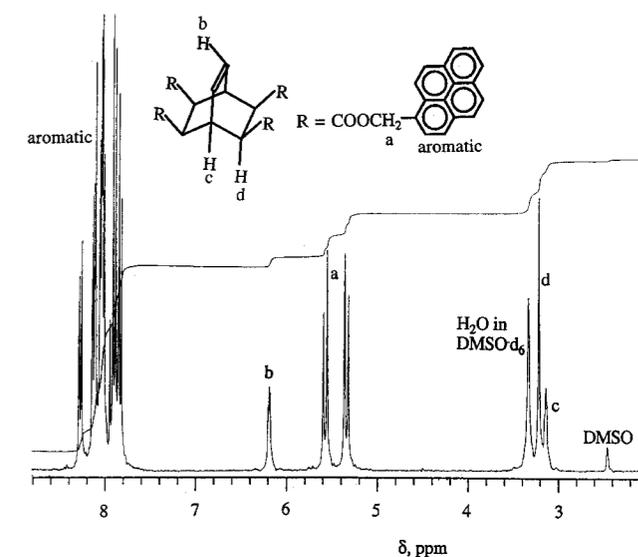
**Figure 1.** Chemical structures of compounds I–VII accompanied by thermal transition data,  $T_g$  and  $\Delta C_p$ , determined for quenched glasses by DSC at a heating rate of 20 °C/min; samples preheated to 200 °C followed by quenching at –200 °C/min to –60 °C.



**Figure 2.** Proton NMR spectrum, 300 MHz, for compound I in CDCl<sub>3</sub>.

groups. Likewise, the fact that a singlet at  $\delta$  5.75 was observed in compound VII indicates free rotation of pyrenyl rings attached to adamantane. If the rotation of pyrenyl rings were hindered, each singlet should be split into a doublet as observed in compound III to be described below.

As we have reported recently,<sup>6</sup> bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid prepared from its dianhydride assumes an all-*exo* configuration, and the ester synthesis under mild conditions of the Mitsunobu reaction is not expected to alter the stereochemistry. As a consequence, one might anticipate that the methylene



**Figure 3.** Proton NMR spectrum, 300 MHz, for compound III in DMSO-*d*<sub>6</sub>.

group connecting the pyrenyl to carboxylate group, as in compound III, should give rise to a singlet. As shown in Figure 3, this methylene group is responsible for two doublets at  $\delta$  5.33 and 5.56 with a coupling constant,  $J_{AB} = 12.3 \text{ Hz}$ , suggesting the magnetic nonequivalence of the two protons, which is believed to arise from the restricted rotation by pyrenyl rings in an all-*exo* configuration. This conclusion was reached based on the observation that the ethyl ester of the same all-*exo*-tetracarboxylic acid, in which the two methylene protons between the methyl and carboxylate group appear as a

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