

Supplementary Information
for
Solvent-Induced Chirality Inversion Involving Supramolecular Helix
Transformation and Color-Tunable Fluorescence of a C_6 -Symmetric
Hexakis(phenylethynyl)benzene Derivative

Koichi Sakajiri,^{*} Takeshi Sugisaki, Keiichi Moriya and Shoichi Kutsumizu

Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193,
Japan

1. Instruments and Materials

Instruments. UV-visible absorption (UV-vis) and circular dichroism (CD) spectra were measured using a Hitachi U-4000S spectrophotometer and a Jasco J-820P spectropolarimeter, respectively. The temperature was controlled with a Komatsu Electronics SPR-7 for UV-vis spectral measurements and a Jasco PTC-423L apparatus for CD spectral measurements. Fluorescence (FL) spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer. The temperature was controlled with a Komatsu Electronics CTE32 apparatus. IR spectra were recorded with a Jasco FT-IR-460 Plus / IRT-30 spectrophotometer.

Materials. Compound L-1 was prepared according to a previously reported method.¹

2. UV-vis, CD, FL and IR Spectra Measurements (Figures 2 – 4, 6 and S1)

Chloroform/*n*-hexane (CHCl₃/Hx) mixtures were mainly used as solvents. UV-vis, CD and FL spectral measurements of 4.20×10^{-5} and 4.20×10^{-6} M solutions were performed at 25 °C in a 1-mm and a 1-cm cell, respectively, except for the FL spectrum in CHCl₃/Hx (100/0) (4.20×10^{-7} M), because the FL intensity saturated at 4.20×10^{-6} M solution. IR Spectral measurement of 4.20×10^{-4} M solution was performed at about 25 °C in a 1-mm cell. In addition, 1,1,2,2-tetrachloroethane/*n*-dodecane (TCE/C₁₂H₂₆) mixtures were also used as solvents. The spectral measurements of the 4.20×10^{-5} M solutions were performed at 25 °C in a 1-mm cell.

3. Computation Method (Figure 5)

UV-vis spectra of a model compound, a hexakis(phenylethynyl)benzene, were calculated using the Spartan'06 programs (Wavefunction, Inc. Irvine, CA)² operated using a PC running under Windows[®] Vista. The calculations were carried out for molecules adopting ten different conformations as a function of dihedral angle β (defined as the torsion angle between the outer benzene rings and the central part of the molecule as shown in the inset of Figure 5), where the β value was varied at 10° intervals from $\beta = 0$ (planar conformation) to 80° and additionally $\beta = 35^\circ$. As a first step, the ten molecules were optimized at the Hartree-Fock (HF) level with the 6-31G* basis set,³ where the β value was fixed and the remaining geometric parameters were allowed to relax fully. Subsequently, for the optimized molecules, single-point excited calculations were performed using time-dependent density functional theory (TDDFT) following ground-state calculations at the DFT level with the B3LYP functional⁴ and the 6-31G* basis set.³ Then, the wavelengths of absorption maxima (λ_{max}) were picked up and plotted against the value of β .

4. References

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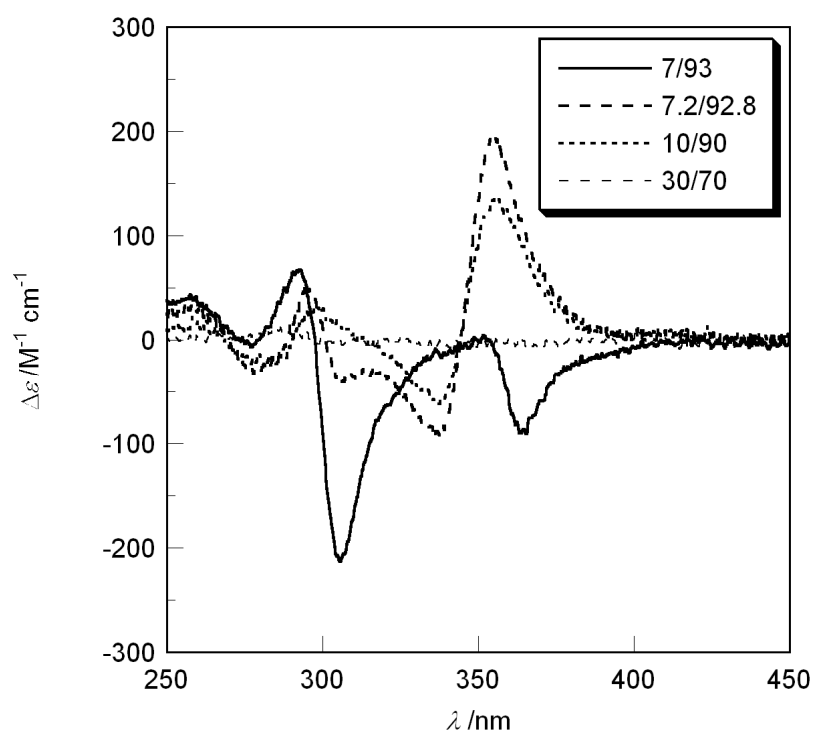


Fig. S1 CD spectra of L-1 (4.20×10^{-6} M at 25 °C) measured in different solvent compositions (CHCl₃/Hx): (7/93), (7.2/92.8), (10/85) and (30/70).

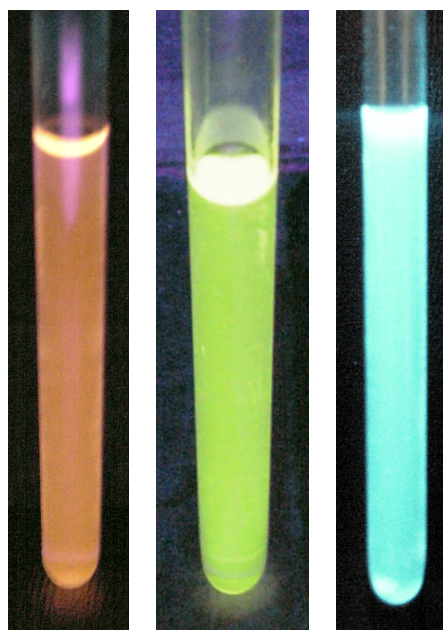


Fig. S2 Photographs of solutions (4.20×10^{-6} M) under UV irradiation at 365 nm: orange in CHCl_3/Hx (5/95); yellow in CHCl_3/Hx (10/90); and light blue in CHCl_3/Hx (100/0).