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Helical naphthodioxepin octamers showing intense CPL in solution and in the solid state

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Circularly polarized luminescence (CPL) is potentially useful in displays, memory, and bioimaging applications because it produces three types of signals: left-handed CPL, right-handed CPL and non-CPL (+, -, and 0). Over the past decade, several organic helical polymers and supramolecules with CPL activity have been developed. Small monomolecular CPL dyes such as helicenes, cyclophanes, and binaphthyl compounds have also attracted attention for use in certain applications. Solid-state CPL is preferred in many applications; however, almost all known monomeric dyes display CPL only in solution. Commercial applications would require novel organic dyes that display much larger solid-state g_{lum} values. In this study, naphthodioxepin octamers (R,R,R,R,R,R,R,R)-1, (R,R,R,S,R,R,R,R)-1, (R,S,R,R,R,S,R,R)-1, and (R,S,R,S,R,S,R,R)-1 were synthesized by a bottom-up method using (R)-BINOL as a starting material. A helically arranged octamer, (R,R,R,R,R,R,R,R)-1 showed intense CPL both in solution and in the solid state. The fluorescence quantum yields (Φ_{FL}) in solution and in the solid state were 0.90 and 0.22, respectively, and the g_{lum} values in solution and in the solid state were $+2.2 \times 10^{-3}$ and $+7.0 \times 10^{-3}$; the Kuhn's anisotropy factor g_{lum} is defined as $2(I_L - I_R)/(I_L + I_R)$, respectively. This is one of the highest solid-state CPL g_{lum} values yet reported. The high Φ_{FL} and g_{lum} values were due to the rigidity as well as to the fact that (R,R,R,R,R,R,R,R)-1 was a non-planar molecule. The π -planes of adjacent (R,R,R,R,R,R,R,R)-1 molecules were incapable of forming efficiently stacked structures due to the non-planar molecular conformation. The signs and the g values of the CPL and the CD related to the transition from the HOMO to LUMO agreed well, as is often the case, indicating that the structures in the ground and excited states were similar. Moreover, VT NMR studies and DFT calculations indicated that the naphthodioxepin octamers were highly stable both chemically and stereochemically.

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