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Stereochemical role of (R,R)-chiral Schiff base Ni(II), Cu(II), Zn(II) complexes and E/Z-azobenzene for polarized light induced supramolecular orientation

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Recently, we have systematically studied linearly/circularly polarized light induced supramolecular alignment of organic/inorganic hybrid materials of azobenzene and chiral Schiff base metal complexes in PMMA or other polymers and some protein biopolymers. Herein, we prepared new chiral Schiff base mononuclear Ni(II), Cu(II), and Zn(II) complexes incorporating all three factors (electron-withdrawing Br-group, UV light-absorbing hydrophobic Ph-group, and hydrogen-bonding HO-groups) in a component complex. Azobenzene caused reversible photoisomerization between trans- (E-) and cis- (Z-) forms after visible light and UV light (continuous wavelength < 350 nm) irradiation within 10 min for the organic/inorganic hybrid materials. When linearly polarized light (with electric vector E) was used, molecular orientation (long axis of the cis-form azobenzene) is aligned perpendicular to E due to Weigert effect, which was detected by polarized spectra as π band at 318 nm and n - π band at 440 nm. Supramolecular interaction propagate ordering of molecular alignment to chiral Schiff base Ni(II) complex exhibiting d-d band at 610 nm and polarized IR C=N band at 1633 cm^{-1} (1628 cm^{-1} for Cu(II); 1617 cm^{-1} for Zn(II)). Gradual CD intensity enhancement as increasing concentration of PMMA acetone solutions also suggests artefact peak for the solid state oriented samples. Stereochemistry of ligands resulted in weakening propagation of optical anisotropy from azobenzene to chiral Schiff base metal complexes in PMMA polymer matrix. Flexibility due to a methylene carbon between the (R)-asymmetric carbon and Ph-group, in contrast to previous analogous chiral Schiff base metal complexes without the methylene group connect (R)-asymmetric carbon and Ph-group directly.

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