Chiroptical Sensing with Molecular and Supramolecular Assemblies

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Chiroptical sensors are an interesting class of compounds that can be used for the selective detection of chemical or biological analytes.[1] The noncovalent interaction between such a system and an analyte (chiral or achiral) results in the characteristic modulation of the circular dichroism (CD) signal, which can be exploited for analytical purposes. Our contribution in the field over the past years has focused on chiral atropoisomeric π-conjugated systems, in particular on 1,1'-binaphthyl units as CD reporters, incorporated into several different classes of supramolecular receptors.[2] We will present recent results about difunctionalized α- and β-cyclodextrin receptors, which can be efficiently capped with π-conjugated axially-chiral units, allowing the development of a new class of cyclodextrin-based chiroptically-responsive receptors.[3] We will also present our work on the use of chiral triptycenes in supramolecular assemblies,[4] and illustrate our approaches to the π-incorporation of dyes such as acridone and quinacridone into their rigid, 3D and potentially chiral scaffolds. We demonstrate that tryptycene-fused benzimidazoles possessing "sleeping chirality," in which several isomers (chiral and achiral) are in equilibrium with each other via imidazole tautomerization can, under controlled experimental conditions, form nanoaggregates with chirality transfer from carboxylic acids through hydrogen bonds, with dissymmetry factors g_{abs} up to $2*10^{-2}$ and g_{lum} up to $6*10^{-3}$, which are among the highest reported for chiral structures self-assembled via hydrogen bonding and the highest for supramolecular systems containing chiral triptycenes.

References:

[1] A. Ozcelik, R. Pereira-Cameselle, N. Ulrih, A. Petrovic, J. Alonso-Gómez, *Sensors* **2020**, *20*, 974.

[2] a) D. Pasini, A. Nitti, *Chirality* **2016**, *28*, 116– 123; b) A. Nitti, D. Pasini, *Adv. Mater.* **2020**, 1908021; c) R. Mobili, G. Preda, S. La Cognata, L. Toma, D. Pasini, V. Amendola, *Chem. Comm.* **2022**, *58*, 3897–3900; d) M. Agnes, A. Nitti, D. A. Vander Griend, D. Dondi, D. Merli, D. Pasini, *Chem. Comm.* **2016**, *52*, 11492– 11495; e) M. Caricato, A. Olmo, C. Gargiulli, G. Gattuso, D. Pasini, *Tetrahedron* **2012**, *68*, 7861– 7866.

[3] G. Preda, S. Jung, G. Pescitelli, L. Cupellini, D. Armspach, D. Pasini, *Chem. Eur. J.* **2023**, in press (Very Important Paper). 10.1002/chem.202302376

[4] a) G. Preda, A. Nitti, D. Pasini, *ChemistryOpen* **2020**, *9*, 719–727. b) G. Preda, A. Aricò, C. Botta, D. Ravelli, D. Merli, S. Mattiello, L. Beverina, D. Pasini, *Org. Lett.* **2023**, *25*, 6490–6494.

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