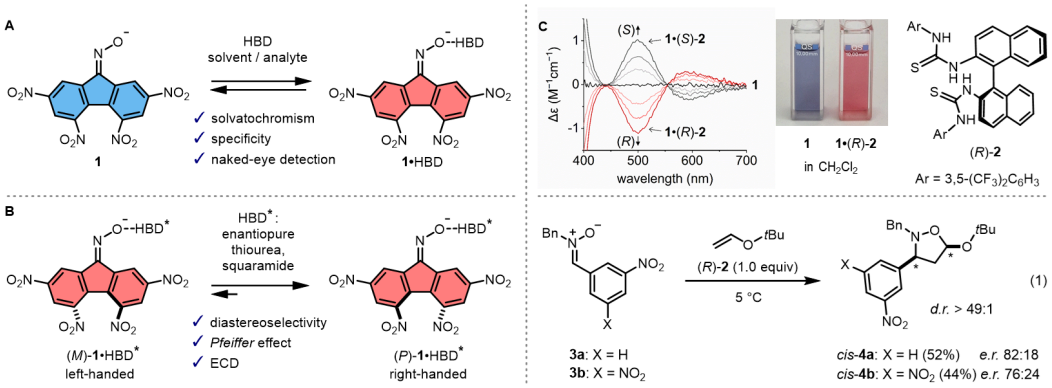
From Naked-Eye Detection of H-Bond Donors to Chiroptical Sensing of Enantiopure Reagents

D. Pál[1], C. Besnard[2], A. I. Poblador-Bahamonde[1], G. Pescitelli[3], J. Lacour[1]*

[1]Department of Organic Chemistry, University of Geneva, Quai Ernest Ansermet 30, 1211 Geneva 4, Switzerland, [2]Laboratory of Crystallography, University of Geneva, Quai Ernest Ansermet 24, 1211 Geneva 4, Switzerland, [3]Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy

2,4,5,7-Tetranitro-9*H*-fluoren-9-one and its derivatives are classical examples of strong *π*-acceptor molecules used in applications from chemistry to industrial and material sciences. Examples include supramolecular nanostructures and removal of aromatic sulfur and nitrogen compounds from diesel fuel based on the formation of charge-transfer complexes. With derivatives containing grafted enantiopure side chains, chiral resolution procedures have been reported, and that of [6]helicene in particular.[1] Herein, in a new development for this class of molecules, we report that readily-accessible oximate **1** presents solvatochromic properties specific to H-bond donors (HBDs), either used as solvents or as individual moieties (Fig. A). In fact, dissolution of dye [Bu_4N][**1**] or [Na][**1**] gives a blue solution ($\lambda_{max} \approx 600$ nm) in aprotic solvents independently of polarity, on the other hand, solvents possessing H-bond donating capabilities are clearly distinguished upon strong hypsochromic shifts ($\Delta\lambda_{max}$ up to −137 nm, blue to red-turning solutions). Notably, an excellent linear correlation was found between λ_{max} of **1** and *Kamlet–Taft* parameter *α* for water and alcohols,[2] linked to their ability to donate a proton in a solvent-to-solute hydrogen bond. As such, water, alcohols, amines, amides, squaramides, thioureas and their different H-bond donating ability can be effectively detected using oximate **1**.



We also demonstrate the existence of helical deformations (twists) within the 2,4,5,7-tetranitro-9*H*-fluorenylidene skeleton and exploit the occurrence of configurationally labile *M* and *P* geometries for the chiroptical sensing (electronic circular dichroism: ECD) of enantiopure reagents: addition of enantiopure thioureas and squaramides to the solution of **1** in aprotic solvents led to remarkable, 50–85 nm hypsochromic shifts in the absorption spectra, accompanied by emerging ECD bands (*Pfeiffer* effect,[3] Fig. B and C) in several instances.

Finally, in an attempt to link ECD chiral recognition and reaction enantioselectivity, the stereoinductions of bis-thioureas onto (i) configurationally labile oximate **1** and (ii) the 1,3-dipolar cycloaddition of structurally related nitrones **3a** and **3b** (eq 1) were compared. The asymmetric induction between bis-thioureas and (*M*)- / (*P*)-**1** served as a direct probing method to select the most effective HBD for asymmetric synthesis.

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