**First hyperpolarizability of the di-8-ANEPPS and DR1 nonlinear optical chromophores in solution. An experimental and multi-scale theoretical chemistry study (arial, bold, 14pt, centered)**

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The solvent effects on the linear and second-order nonlinear optical properties of an aminonaphtylethenylpyridinium (ANEP) dye are investigated by combining experimental and theoretical chemistry methods. On the one hand, deep near infrared (NIR) hyper-Rayleigh scattering (HRS) measurements (1840–1950 nm) are performed on solutions of di-8-ANEPPS in deuterated chloroform, dimethylformamide, and dimethylsulfoxide to determine their first hyperpolarizablity (bHRS). For the first time, these HRS experiments are carried out in the picosecond regime in the deep NIR with very moderate (≤3 mW) average input power, providing a good signal-to-noise ratio and avoiding solvent thermal effects. Moreover, the frequency dispersion of bHRS is investigated for Disperse Red 1 (DR1), a dye commonly used as HRS external reference. On the other hand, these are compared with computational chemistry results obtained by using a sequential molecular dynamics (MD) then quantum mechanics (QM) approach. The MD method allows accounting for the dynamical nature of the molecular structures. Then, the QM part is based on TDDFT/M06-2X/6-311+G∗ calculations using solvation models ranging from continuum to discrete ones. Measurements report a decrease of the bHRS of di-8-ANEPPS in more polar solvents and these effects are reproduced by the different solvation models. For di-8-ANEPPS and DR1, comparisons show that the use of a hybrid solvation model, combining the description of the solvent molecules around the probe by point charges with a continuum model, already achieves quasi quantitative agreement with experiment. These results are further improved by using a polarizable embedding that includes the atomic polarizabilities in the solvent description. (arial, 11pt, justified)

**References [**arial, 10pt, spacings: 1 pt before and 1 pt after, line spacing 12pt**]**

C. Bouquiaux *et al.*, J. Chem. Phys. **159**, 174307 (2023).

T. Verbiest *et al.* *Second-Order Nonlinear Optical Characterization Techniques: An Introduction*, Taylor & Francis (2009).

Max. 1 A4 page; margins of 2 cm, spacings: 3 pt before and 3 pt after, line spacing 15pt (except the title 18pt); max. 3 references, max 1 figure, no table.