Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Toward a Microscopic Model of Light Absorbing Complex Organic Components in Aqueous Environments: Theoretical and Experimental Study.

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This PDF file includes:

Figures S1 to S8

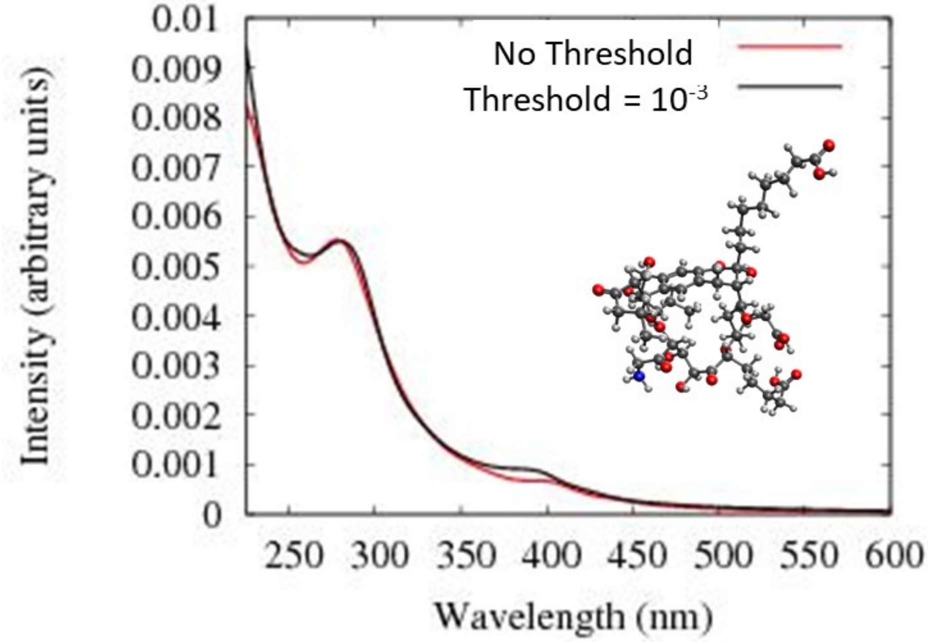
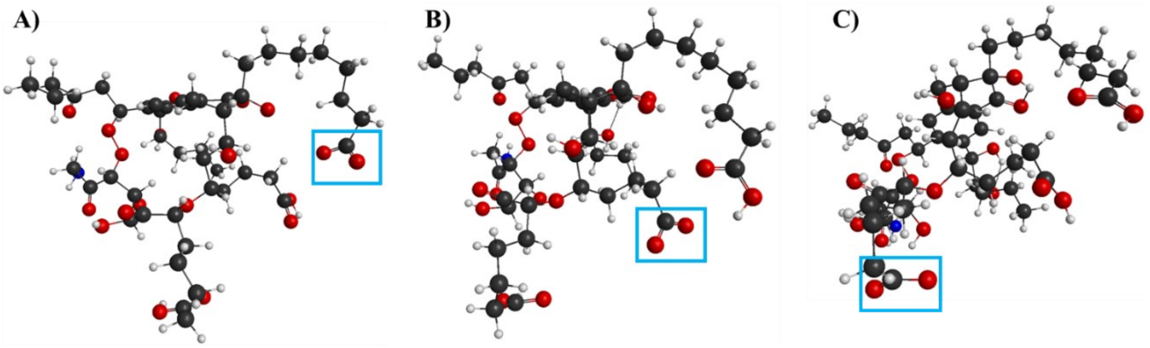


Fig. S1. Optical absorption spectra of selected structure $C_{48}O_{19}N_1H_{73}$ in gas phase with and without threshold.



$(C_{48}O_{19}N_1H_{72}^-)\cdot(H_2O)_{100}$ (**v1**) $(C_{48}O_{19}N_1H_{72}^-)\cdot(H_2O)_{100}$ (**v2**) $(C_{48}O_{19}N_1H_{72}^-)\cdot(H_2O)_{100}$ (**v3**)

Fig. S2. Structures of ionized m-CDOM models $(C_{48}O_{19}N_1H_{72}^-)\cdot(H_2O)_{100}$ (water molecules are not shown). Blue square was used to mark the position of $-COO^-$ group.

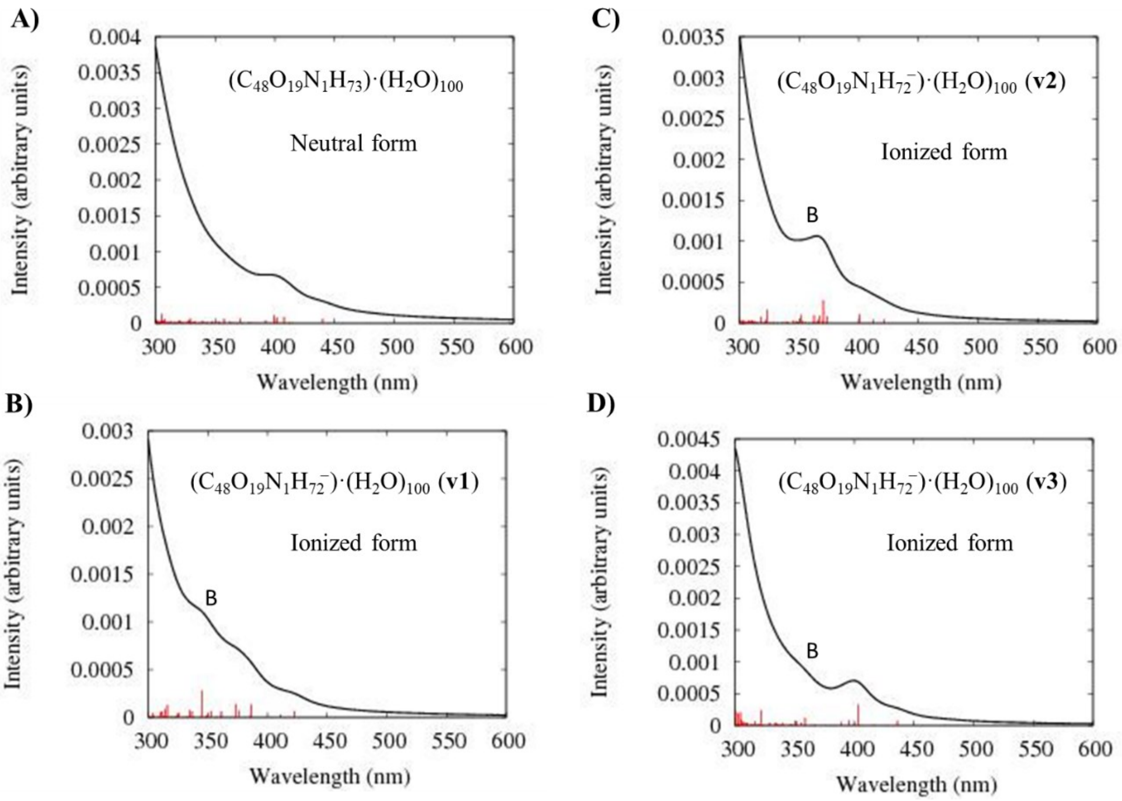


Fig. S3. Theoretical optical absorption spectra (region 300-600 nm) of : (A) neutral structure $C_{48}O_{19}N_1H_{73}\cdot(H_2O)_{100}$, (B) the ionized form $(C_{48}O_{19}N_1H_{72}^-)\cdot(H_2O)_{100}$ (**v1**), (C) the ionized form $(C_{48}O_{19}N_1H_{72}^-)\cdot(H_2O)_{100}$ (**v2**), and (D) the ionized form $(C_{48}O_{19}N_1H_{72}^-)\cdot(H_2O)_{100}$ (**v3**).

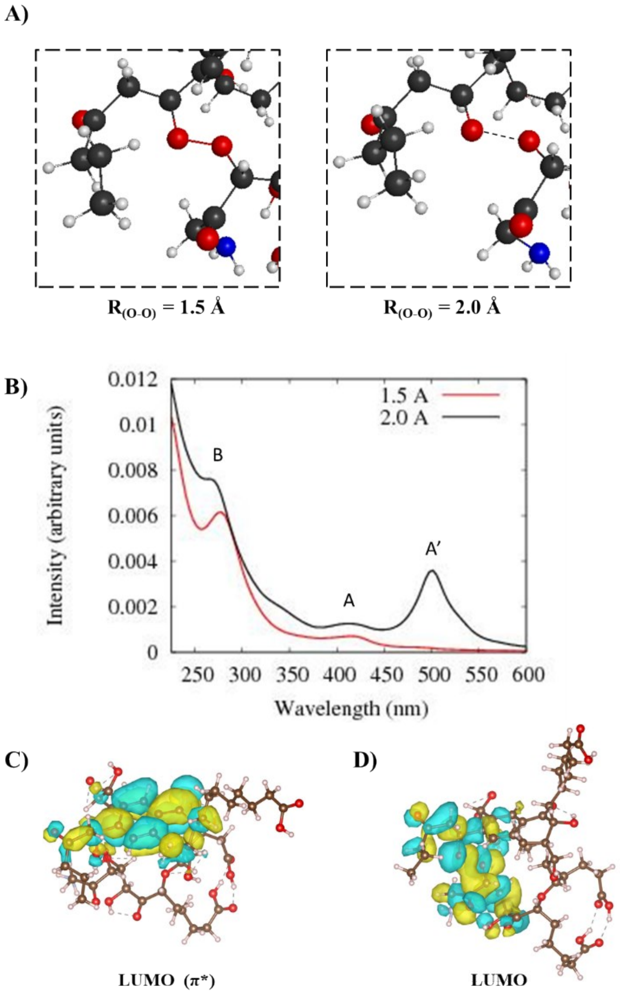


Fig. S4. (A) fragments of structures of $C_{48}O_{19}N_1H_{73}$ in gas phase with $R_{(O\text{-}O)}$ = 1.5 and 2.0 Å; (B) optical absorption spectra of these structures with $R_{(O\text{-}O)}$ = 1.5 and 2.0 Å; (C) LUMO orbitals of structures with $R_{(O\text{-}O)}$ = 1.5 Å; and (D) LUMO orbitals of structures with $R_{(O\text{-}O)}$ = 2.0 Å..

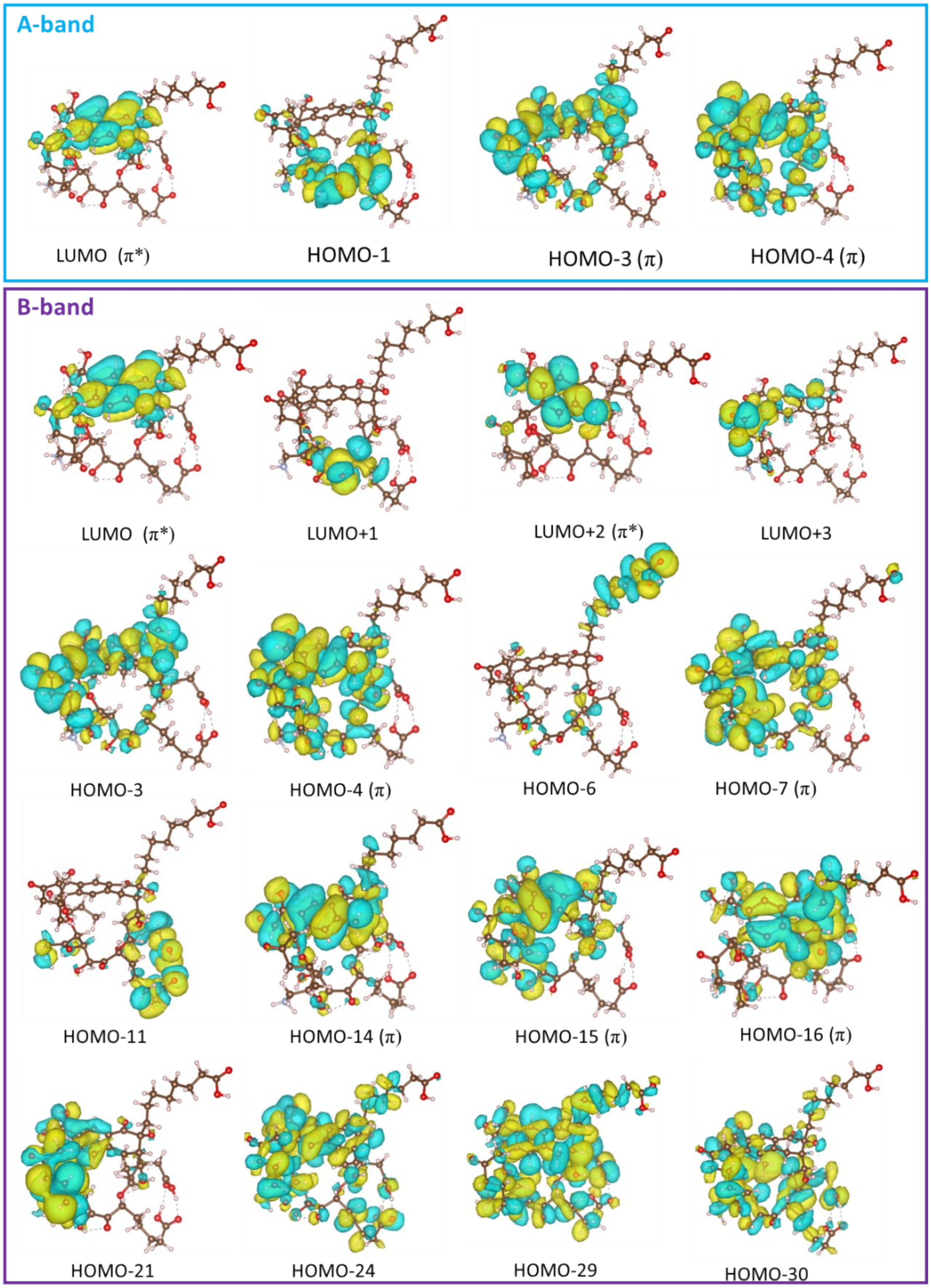


Fig. S5. Selected orbitals of the structure $C_{48}O_{19}N_1H_{73}$ responsible for the formation of A- and B-bands.

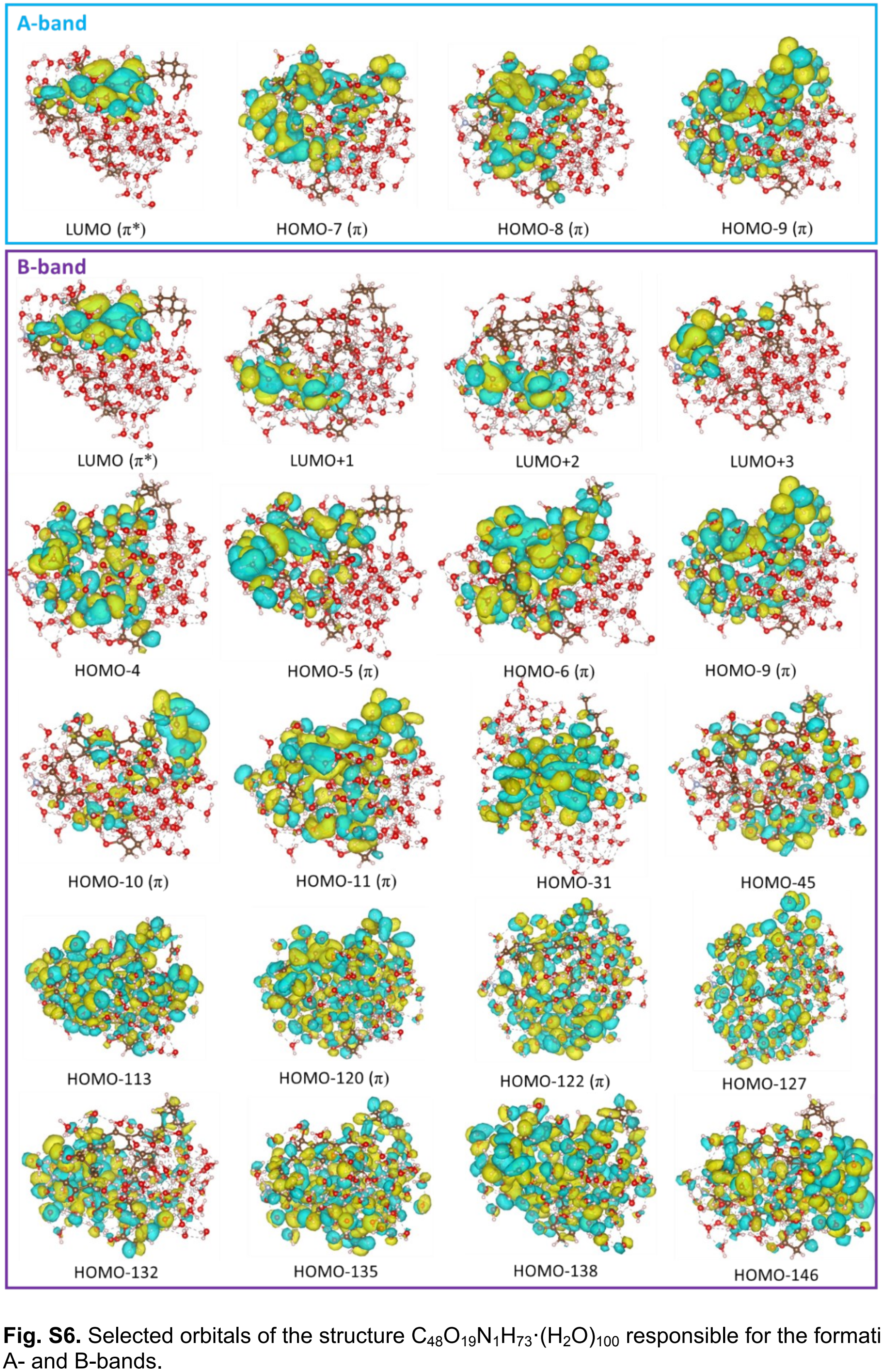


Fig. S6. Selected orbitals of the structure $C_{48}O_{19}N_1H_{73}\cdot(H_2O)_{100}$ responsible for the formation of A- and B-bands.

Solvent Models Justification

Two types of solvent model systems were considered: (1) combination of a small amount of explicit water molecules with the polarizable continuum model, and (2) a large amount of explicit water molecules around the chromophore. These two models were tested in our calculation and compare with experiment for 4BBA, which is smaller than the molecule consider here but it is never the large enough to provide the realistic test.
The results on these two models are discussed below:

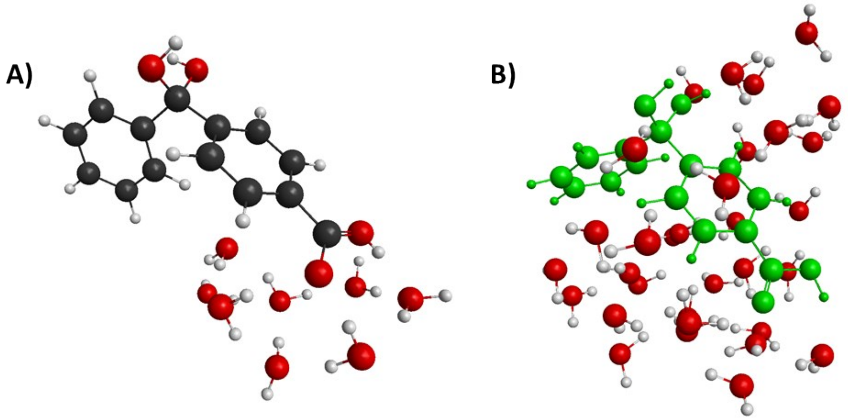


Fig. S7. Neutral diol-form of 4BBA coordinated by: (a) 8 and (b) 30 water molecules**.**

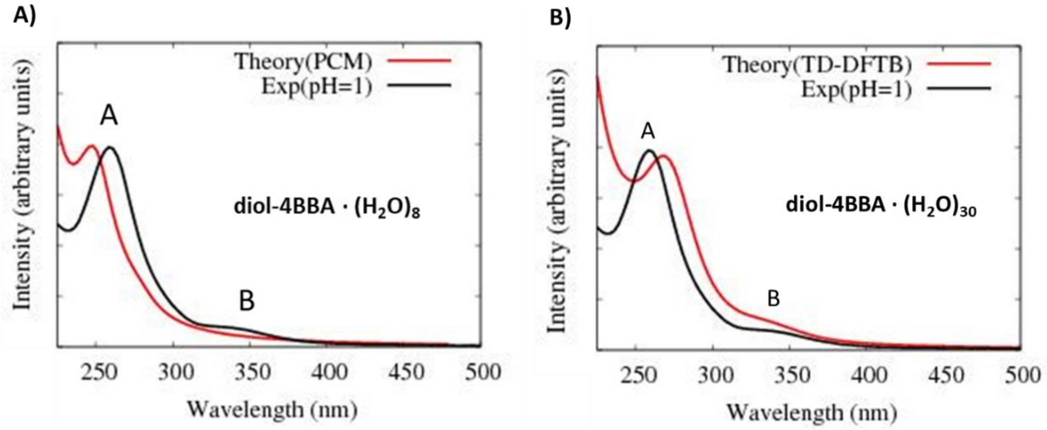


Fig. S8. Optical absorption spectra of neutral diol-form of 4BBA: (a) 8 explicit water molecules + PCM (B3LYP/6-311++G**), and (b) 30 explicit water molecules (DFTB calculations).

Solvent Model 1 (the combination of explicit and Implicit water molecules). All theoretical calculations for clusters 4BBA·$(H_2O)_8$ were performed using Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) methods within Q-Chem program.[1] Geometry optimizations employ the B3LYP functional[2] and basis set 6-31+G*, with dispersion corrections from Grimme's DFT-D2.[3] For calculations of excited states, the explicit solvent molecules (water clusters in our suggested models) were combined with the polarizable continuum model (C-PCM)[4]. Solute cavities are constructed from a union of atom-centered spheres whose radii are 1.2 times the atomic van der Waals radii suggested by Bondi.[5] The C-PCM was employed in combination with B3LYP/6-311++G** method. This approach was previously successfully used for the simulation of benzoic acid.[6] For each excitation energy, the vertical transitions were convoluted with a Lorentzian line shape with a width of 20 nm, and all of the resulting Lorentzians were added to yield the excitation spectrum.

Obtained results showed that the theoretical spectrum of neutral diol-form of $4BBA{\cdot}(H_2O)_8$ do not able to mimic the shape of the experimental curve of 4BBA at low pH (**Fig. S7a, S8a**). This simulated spectrum does not have the experimental B-band in the low-energy region. Overall, considered model systems with 8 water molecules cannot be used for reproducing the experimental data of large organic molecules with different functional groups. Even the additional solvent effects, such as the polarizable continuum model (C-PCM) do not make any significant changes. The problem can be addressed to the interactions of water molecules with diol-groups of 4BBA, which were not considered in the small models with 8 water molecules. Therefore, in the next step, the larger water clusters will be considered to simulate the interactions of the carboxy-, and diol-groups of 4BBA system with water molecules.

Solvent Model 2 (significant amount of explicit water molecules only $4BBA{\cdot}(H_2O)_{30}$). To include the interactions all functional groups presented in 4BBA molecule (diol- and carboxy-groups) with solvent media, large water clusters (30 water molecules) were considered using the density functional tight-binding (DFTB) method[7] and excited states formalism TD-DFTB,[7,8] which aims to achieve the accuracy of DFT methods and the efficiency of tight-binding-based methods.

Our calculation showed that large explicit water clusters provide much more correct improvement with the experiment than it was obtained by relatively few explicit molecules supplemented by the continuum model: both experimental A- and B-bands were reproduced (**Fig. S7b, S8b**).

The results are not surprising because the microscopic interactions for a large number of explicit solvent molecules are expected to be much more realistic than the continuum model can provide.

Therefore, solvent effects are very important for reproducing the correct optical spectra of a relatively large organic molecules with different types of functional groups in the water environment.

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