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Response to Comment "On the Existence of Excitonic Signatures in the Optical Response of Metal–Organic Frameworks"

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This is a response to a comment on the interpretation of the origin of the nonlinear changes of optical properties of van der Waals' metal–organic frameworks (MOFs). The concerns are addressed by clarifying potential pitfalls in density functional theory (DFT) simulations, careful analysis of prior literature, and additionally discussing the previous experimental results to emphasize the applicability of the excitonic concept in molecular crystals, such as MOFs.

In our recent paper,[1] we demonstrated the possibility of all-optical data processing and storage using a layered van der Waals' metal–organic framework (MOF) ($[\{Zn_2(TBAPy)(H_2O)2\}\cdot 3.5DEF]_n$ (**1**) (TBAPy, 1,3,6,8-tetrakis(p-benzoate)pyrene; DEF = diethylformamide). The optical properties of **1** could be efficiently and independently manipulated via light-induced local crystal disordering or ultrafast/continuous wave (cw) photoexcitation. A reversible structural response resulting in the nonlinear changes of the optical properties was achieved on an ultrashort timescale and could be preserved for several days. We proposed that such a behavior is due to the synergistic combination of the well-defined organic–inorganic nature of **1** and its anisotropic layered structure that gives rise to two different types of robust excitons (interlayer and intralayer). The assignment of the observed optical features to the excitons was done based on the fundamental principles of molecular excitons extensively described in the last 50 years in books,[2] reviews[3a-c] and research papers;[3d-l] and supported by complex transmission, reflectance, and photoluminescence (PL) spectroscopy with polarization and time resolution.

Polozkov et al.[4] made a comment to dispute our assignment of the optical features to excitons, based on the results of electronic structure calculations carried out using the generalized gradient approximation Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional on a simplified 2D periodic model of a single layer of **1** (**Figure 1**). Despite the severe oversimplification of the actual system in the model and the known limited accuracy of pure exchange-correlation functionals for describing excitations in molecular systems,[5] the authors obtained a nearly quantitative agreement between the computed and experimentally observed features in the absorption spectrum. Given the intrinsic limitation of the time-dependent density functional theory (DFT) method to single-particle excitations and its fundamental inability to describe excitonic states, these results motivated the authors to question our interpretation of the experimental data and propose an alternative model that is solely based on a single-particle approximation. We do not agree with the new proposal and identify a number of critical flaws in the logics underlying the comment. Below we provide extensive argumentation supporting our viewpoint.

First of all, we believe that the coincidence between a computed parameter and an experimental one cannot be used as a justified ground for the construction of a physical or chemical hypothesis without a critical assessment of the potential limitations related to the accuracy of both the model and the method employed in the calculations. The method accuracy in this context can be better viewed as the precision of the calculation – that is, how well a particular quantum chemical method describes the electronic structure and basic parameters of chemical systems; and it is commonly assessed against a back-drop of a desired well-defined outcome.[6] Modern quantum-chemical methodologies are suitable for resolving ground-state chemical phenomena with <4 kJ mol^{-1} absolute accuracy, which is often referred to as the "chemical accuracy".[6c] However, when dealing with such complex systems as the metal–organic frameworks, this high

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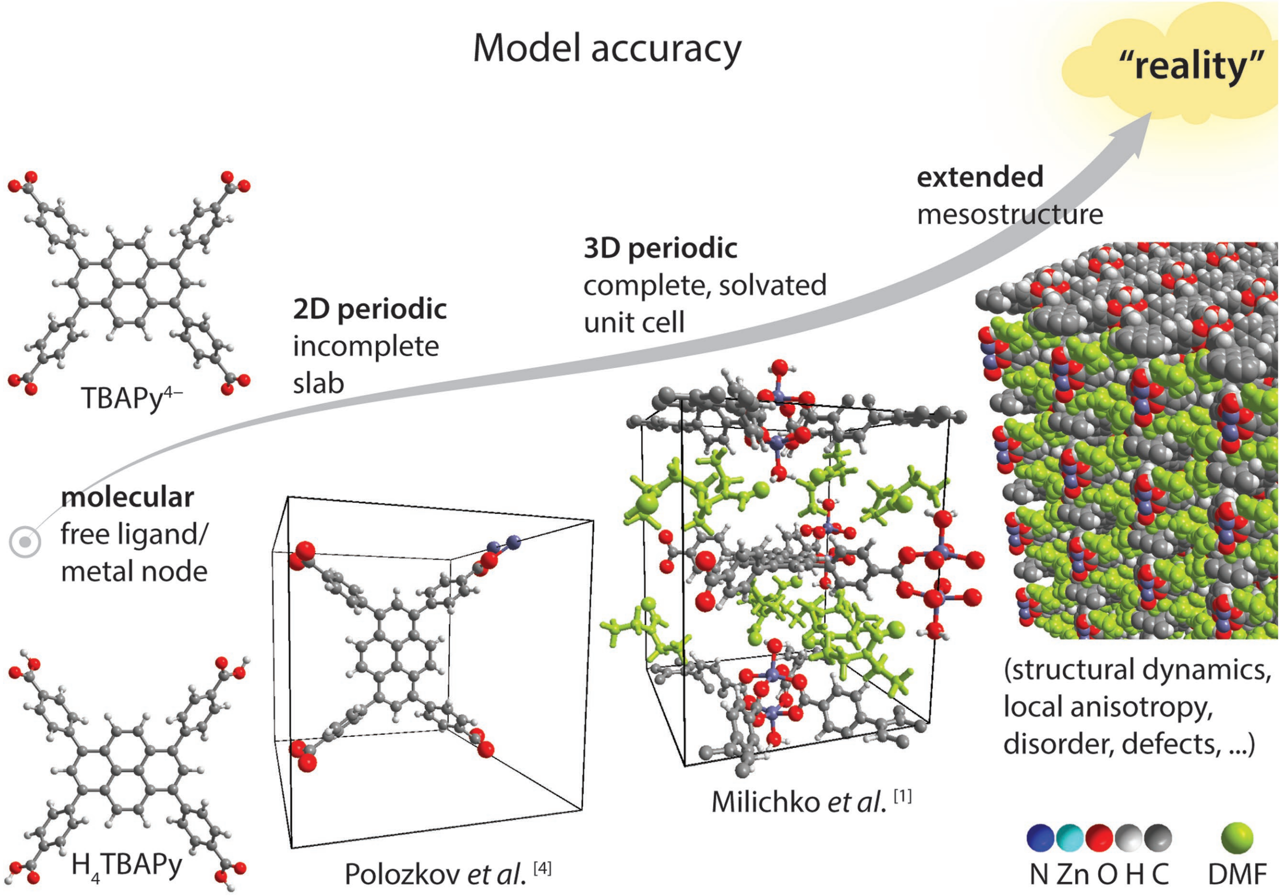

Figure 1. Evolution of the model accuracy for different atomistic models of Zn-MOF, where the lowest level approximation (molecular) is the individual components of the MOF, followed by a 2D periodic slab model representing a single Zn-MOF with an incomplete coordination sphere of Zn centers and a chemically accurate 3D periodic unit cell with an experimentally-relevant chemical composition representing the crystal structure of Zn-MOF containing DMF solvent in the interlayer space, and a hypothetic extended mesoscale model that could potentially account for the structural anisotropy and interlayer dynamics of the actual chemical system.

computational precision can almost never be achieved along with the realistic representation of the actual chemistry of the models. The accuracy of a model is therefore a system-specific parameter, which in some cases may represent a highly complex multidimensional problem encompassing a wide variety of factors and physicochemical phenomena. In practice of computational chemistry and material sciences, one cannot achieve the highest method precision along with the chemically accurate definition of the model. One will always have to search for a compromise between these two parameter spaces to balance the model and the method accuracy. Both of them need to be sufficiently accurate to describe the physical and chemical phenomena in question.[7] We find that both the model and the method employed by Polozkov et al.[4] do not satisfy this requirement to allow an adequate description of the current MOF chemical system and the associated optical effects.

The experimental studies described in our original paper[1] deal with the optical characteristics of macroscopic van der Waals' MOF crystals that stem from the substantial structural dynamics and local anisotropy manifested at the mesoscale. Note that such phenomena cannot be captured even by using the chemically accurate periodic 3D models employed in our original study (Figure 1). Polozkov et al.[4] in their comment further simplified this model to be able to carry out the rather demanding time-dependent (TD-DFT) calculations. Besides omitting the details of the 3D structure, which was proposed to be crucial for the unique optical effects observed in the experiment, the authors used a chemically incomplete model of the individual slab containing undercoordinated Zn^{2+} nodes lacking the structural H_2O ligands.

Even with such severe model simplifications, the size of the chemical structure was still too large to advance beyond the GGA approximation in the electronic structure and excited state calculations. However, previous extensive benchmark studies have demonstrated the inability of pure exchange-correlation functionals to accurately predict excited state properties of even well-defined systems.[5] It is explicitly stated in the review by Adamo and Jacquemin that "...one should avoid applying pure (i.e., exact-exchange free) functionals as they tend to significantly undershoot the transition energies in the majority of organic and inorganic systems. Go for hybrids: transition energies will be closer to the experimental spot, with an expected error range of 0.20–0.25 eV".[5] They further note that physically meaningful description of the charge transfer or Rydberg

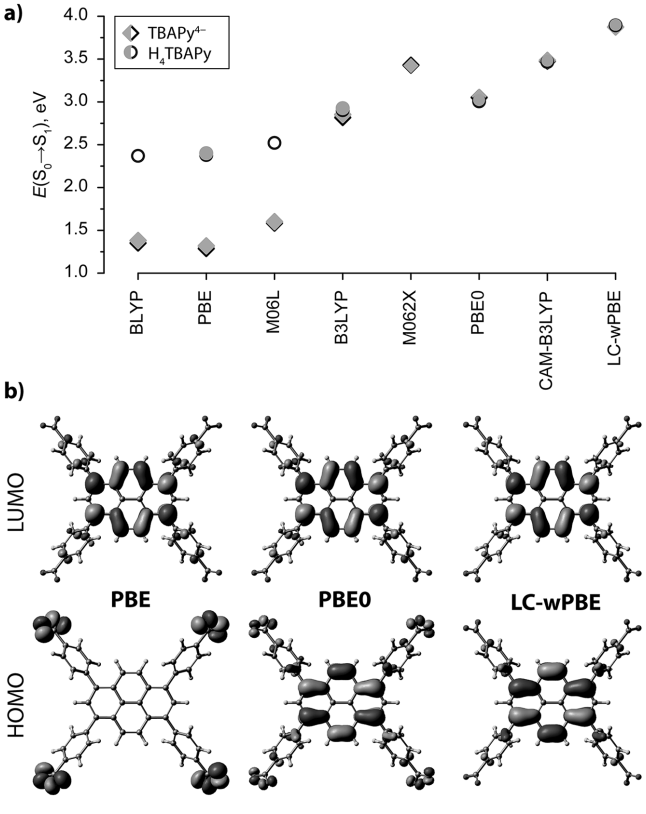

Figure 2. a) Results of TD-DFT calculations (first excitation energy) on the free ligand in the protonated (H_4TBAPy) and cationic ($TBAPy^{4-}$) forms carried out using different DFT methods in combination with 6–31+G(d,p) (open symbols) and 6–311+G(d,p) (closed symbols) basis set. b) The corresponding frontier orbitals produced by DFT methods of a single family but belonging to different rungs of the DFT accuracy ladder.

electronically excited states would require the use of the range-separated hybrid functionals.[5]

To illustrate the importance of the balance between the model definition and the method accuracy, we carried out a series of TD-DFT calculations on the excessively reduced minimal model for the current MOF, which is the isolated ligand in the protonated (H_4TBAPy) and cationic ($TBAPy^{4-}$) forms using a range of popular DFT methods. The results, summarized in **Figure 2**, reveal a strong impact of the nature of the exchange-correlation functional on the predicted energy of the single-particle transition (highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) (Figure 2a)). In line with earlier benchmark studies, pure functionals (BLYP, PBE, and M06) predicted much lower excitation energies for both models compared to their hybrid counterparts. The HOMO–LUMO excitation energy for H_4TBAPy computed with the GGA and meta-GGA methods is "only" ca. 0.5–1 eV off the values predicted by the more accurate hybrid and long-range corrected hybrid functionals. More importantly, the GGA results are strongly model-dependent. Whereas the hybrid methods predict similar excitation energies for the anionic ($TBAPy^{4-}$) and protonated (H_4TBAPy) ligand, pure functionals give much lower excitation energies for the anionic form. This finding is particularly important given the ionic nature of the bonds between the Zn^{2+} cations and carboxylate ligands in the actual MOF structure. The analysis of the frontier orbitals computed using different DFT methods reveal that this result is due to the strong electron delocalization errors in the GGA calculations (Figure 2b).[8] This effectively implies that the chemical inaccuracies of the model combined with the incomplete geometry optimization by Polozkov et al.[4] could potentially introduce additional substantial errors to the results of the already quite inaccurate TD-DFT calculations at the PBE level.

We conclude that the exact correlation between the numerical outcome of the TD-DFT (PBE) calculations and the experimentally observed excitation energy cannot be used as an argument for its assignment to a classical HOMO–LUMO transition. Depending on the choice of the exchange-correlation functional, the results of TD-DFT calculations may shift within a margin of over 2 eV. The nearly quantitative agreement between theory and experiment emphasized by Polozkov et al.[4] points rather to the imperfections of the methodologies and the models than serves as a good basis for an alternative scientific hypothesis.

Regarding the assignment of the current nonlinear optical phenomena to excitons, it is well-known that they are central to describe generic optical processes in single molecules, molecular aggregates, and molecular crystals, such as photoinduced electron transitions,[2,3] photosynthesis,[9] photovoltaic response,[10] and optical communications.[11] These states are directly related to single-particle transition in molecules and just slightly modify its shape.[2f,3a,f,12] As a result, there is a sufficient identity between the shapes of the exciton states and HOMO–LUMO transition in the absorption spectrum as Polozkov et al.[4] clearly mentioned in the comment. However, there are several fundamental differences between the excitons and single-particle transitions that we experimentally demonstrated.[1]

First of all (Figure 3 in ref. [1]), the probability of single-particle dipole transitions is proportional to $(\cos \alpha)^2$ where α is an angle between the vectors of polarization of light and transition dipole moment. No frequency shift of the maximum of absorption should be observed. In our case, we detected a frequency shift from 2.95 to 3.2 eV when α changes from 0 to 90° evidencing the transition to two different electronic states in **1**. We assign these states to different type of excitons having the dipole moments along or perpendicular to the layers of **1** (intra and interlayer ones).

Second (Figure 2c in ref. [1]), the PL in the blue region (2.77 eV) has a very spatially inhomogeneous picture (**Figure 3**, inset), which is a direct demonstration of the radiative recombination of excitons[13] on crystal defects or PL from the exciton liquid within the homogeneous substrate. In contrast, the PL from single-particle transitions normally demonstrates a spatially homogeneous picture independently of the degree of inhomogeneity of the substrate. In our case, we attribute the spatially inhomogeneous PL to the defects because of the highly defected nature of the MOF crystals fabricated by a solvothermal method.[14] Furthermore, the formation of an exciton liquid requires a higher concentration of excitons than we had in our experiments (see below). These two important issues were completely neglected in the comment, resulting in a dubious conclusion about the nature of optical nonlinearities.[1]

In addition, we would also like to critically discuss several important fundamental proposals made in the comment regarding: i) the binding energy of the interlayer excitons,

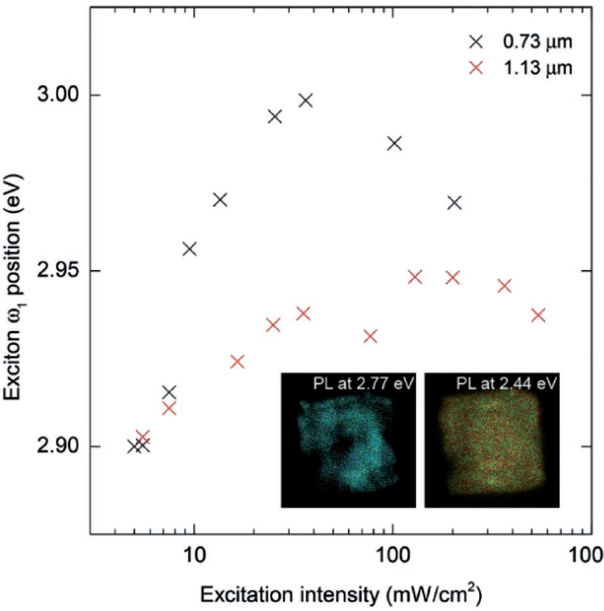

Figure 3. Blueshift of the interlayer exciton ω_1 position with increase of excitation intensity of a white light. The data were obtained by fitting the absorption spectra and are described in Supporting Information of ref. [1]. The error for each point is 0.025 eV. Inset: PL map of the single crystal of **1** at different emission energy (2.77 and 2.44 eV) illustrating a strong spatial inhomogeneity for the exciton radiative recombination at 2.77 eV for 0.8 ns, while 4 ns PL from pure organic components at 2.44 eV is clearly homogeneous.

ii) the Mott transition in the excitonic system, and iii) exciton transport as a direct demonstration of the excitonic nature.

i) The discussion about the need of a higher radius for the interlayer exciton is inconsistent in our case because the distance between the layers is less than 9 Å, which is sufficiently smaller than the size of the TBAPy ligand (≈18 Å), in which the intralayer exciton is generated (see Figure S1 of the Supporting Information in ref. [1]). If the dimension of the layers is comparable to the radii of both excitons, the dielectric permittivities become similar for the orthogonal directions. For the conventional, pure, inorganic van der Waals' materials, a smaller binding energy of interlayer excitons is commonly observed.[15] However, this does not apply to the hybrid MOF material **1** giving rise to the higher binding energy for the interlayer excitons.

ii) The exciton transitions normally have very large oscillation strength so that a small number of excitons provides sufficient changes of dielectric permittivity of the matter. With such transitions, the dependence of the absorption/PL on the excitation intensity becomes highly nonlinear; that is, the increase in excitation intensity is first accompanied by the expected increase of absorption/PL, which is then followed by its decline (observed for interlayer exciton ω_1 at 2.95 eV (Figure 4 and Figure S5e in ref. [1])). A similar nonlinear behavior was experimentally and theoretically demonstrated for other excitonic systems.[16] The decreasing absorption for intralayer excitons (3.2 eV)[1] is still a matter of debate and requires further kinetic analysis. Another plausible explanation of such a nonlinear absorption/PL behavior can be found in experimental and theoretical studies devoted to exciton–exciton annihilation with blueshifted excitons (Figure 3), the effect of temperature on the interlayer exciton, and to the formation of the exciton complexes.[17] All these processes require respectively high exciton concentration. Concerning the Mott transition in exciton systems,[18] such an effect is only at a critical exciton concentration (N_c) which is equal to $r_{er}{}^{-3}$, where r_{ex} is an exciton radius. In our case, N_c is equal to 10^{25} m^{-3}, and the achieved concentration in the experiments is lower than 10^6 m^{-3} due to the low excitation intensity (up to 0.1 W cm^{-2}, see Figure 4 in Ref. [1]). The exciton concentration was estimated by the following equation $N = P\alpha(I\tau/c\hbar\omega)$, where P is the probability of exciton generation, α is the absorption coefficient, I is the excitation intensity, τ is the exciton lifetime, c is the speed of light, and $\hbar\omega$ is the energy of the photons.

iii) Finally, we disagree with the statement made in the comment on the need of the demonstration of energy transport to identify excitons. This approach is efficient only for the excitons with a high lifetime normally found in defect-free materials[19] at low temperature. It is well known that excitons exist within low-dimensional systems (quantum dots, quantum wells) and nanocrystals at ambient condition, where their movement is spatially limited and quantized. Moreover, there are excitons within bulk matter having a lot of crystal defects, which provide exciton localization and self-trapping. To identify the excitonic phenomena in different materials, one should test other optical effects described in ref. [17e].

In summary, the comment raises a problem of describing the nature of optical effects in organic–inorganic materials, which is very important for the development of new applications of such materials. In the case of layered van der Waals' metal–organic frameworks, the extensive experimental data[1] and theoretical/experimental results from other groups[2,3,5–20] allow us to confidently assign the observed optical phenomena to excitonic transitions supporting the original proposal on the principle possibility of the all-optical data processing and storage in **1**.

Experimental Section

Electronic Structure Calculations: All DFT calculations were carried out using the Gaussian 09 rev. D.01 program package.[20a] Full geometry optimizations were carried out for all levels of theory and ligand models prior to the analysis of the electronic structure and the calculation of the optical properties. For all the optimized structures, the nature of the stationary points was evaluated from the analytically computed harmonic modes. No imaginary frequencies were found for the optimized structures confirming that they correspond to local minima on the potential energy surface. The calculations were carried out using a selection of popular exchange-correlation functionals corresponding to different "rungs" on the "DFT accuracy ladder", namely, the pure GGA BLYP,[20b,c] PBE,[20d,e] and meta-GGA M06L[20f] functionals, hybrid B3LYP,[20f] PBE0,[20g] and M062X[20h] functionals, and the long-range corrected CAM-B3LYP[20h] and LC-wPBE[20] methods. The calculations were performed with 6–31+G(d,p) and 6–311+G(d,p) all-electron basis sets on all atoms. Excited-state calculations were carried out in the framework of the linear-response time-dependent density functional theory.[5]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

accuracy, density functional theory, excitons, metal–organic frameworks, molecular modeling

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