



Immobilization of UiO-67 with photochromic spiropyrans: a quantum chemical study

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Abstract

Post-synthetic modification of MOFs allows tuning the properties according to desired applications. The incorporation of photoactive molecules introduces sensitivity to radiation properties to the matrix of MOFs. We report on the theoretical analysis of possible ways of construction photoactive MOFs from UiO-67 and spiropyran molecules containing different carbonyl substituents. Large-scale computer modeling with the use of density functional theory method allowed us to select the most energy-efficient schemes of design. It was revealed that the most preferred way of immobilization of UiO-67 is the interaction with the carboxylic group in the indoline fragment of spiropyran. These results are promising for the application of MOFs modified in this way as photoactive sensors.

Keywords MOF · Metal-organic framework · Functionalization · Spiropyran

Introduction

Metal-organic frameworks (MOFs) are porous materials with high specific surface area and tunable properties [1–3]. Their 3D framework could be conditionally divided into organic and inorganic parts [4, 5]. Inorganic units or, as named, secondary building units (SBUs) are inorganic polynuclear clusters, contained metal ions [6]. They are stitching together with organic linkers by strong covalent bonds. Various combinations of SBUs and linkers lead to structures with specific properties. Linkers design results in frameworks with desired size and shape of pores and allowed to decorate pore surface with functional groups, while the incorporation of specific metals into SBUs allowed tuning such properties as the flexibility of structure, magnetic, and catalytic properties [7–13]. This feature makes MOFs extremely popular for the design of hybrid materials [14–17].

In 2008, Karl Petter Lillerud and coworkers reported on a new family of MOFs with exceptional thermal and chemical stability—UiO (stands from University of Oslo) [18]. SBUs in UiO MOFs are hexanuclear zirconium clusters $Zr_6O_4(OH)_4$; each SBU is bonded with 12 linkers [19–22]. A combination of $Zr_6O_4(OH)_4$ SBU with a 4,4-biphenyl-dicarboxylate (BPDC) linker leads to the formation of isorecticular UiO-67 with two types of pores—tetrahedral (12 Å) and octahedral (16 Å) [19]. Large cages and high stability make UiO-67 popular material for further functionalization. Particularly, localization of spiropyran (SP) molecules in the UiO-67 cages provides photoactive properties to the resulting hybrid material. Recently it was reported that embedding of SP in UiO-67 cages did not obstruct the photoactive properties of the organic molecule [23]. Under UV irradiation, the SP molecules inside UiO-67 pores reversibly isomerize to the open merocyanine form. In this way, the conductance of composite material can be increased by one order of magnitude. In this report, the authors used the soaking of UiO-67 film by SP solution to produce hybrid material. Although this technique is rather simple, it could have serious limitations. SP molecules could localize only on the surface of MOF particles, which will significantly reduce the potential of such systems as sensors.

In the present work, we propose a theoretical analysis of the other functionalization technique—the partial substitution of linkers with SP molecules. According to this method, SP

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molecule will bond with Zr^{4+} ions from SBU, which will result in controllable saturation of the UiO-67 substrate with photoactive molecules and retain these SP molecules by strong covalent bonds instead of trapping on the MOF cages. For the successful application of this technique, the SP molecule should provide functional groups, which form strong bonds with zirconium. The most suitable are carboxylic ones capable of forming a coordination node, similar to that found in UiO-67.

Methods

Quantum chemical calculations were applied to clarify the correctness of the proposed model—UiO-67 (1) functionalized with spiropyran molecules containing suitable donor groups. The study was performed within the density functional theory method using the B3LYP functional and the Def2-TZVP extended basis set. U-67 model is constructed from SBU with six zirconium ions and 12 linkers reduced to benzoic acid. Spiropyran (2)–(4) containing a carboxyl group in the 5-position of the indoline fragment are considered as starting compounds. The position 6' of the 2H-chromene fragment of these compounds is occupied by the nitro group (2) ($R_1 = NO_2$, $R_2 = H$), which is part of the spiropyran considered in [23]. Compound (3) similar to described earlier [24] contains *o*-hydroxyaldehyde fragment at positions 6' and 7' ($R_1 = CHO$, $R_2 = OH$) while spiropyran (4) is modified by second 6'-carboxylic group ($R_1 = COOH$, $R_2 = H$). Consideration of systems with additional chelating fragments will allow evaluating the ambidentate properties of spiropyran (3) and (4) and revealing the most promising way of modifying UiO-67.

The following questions were considered in the present work:

- Is the process of replacing mono-anionic spiropyran with a benzoic acid residue thermodynamically advantageous?
- What method of coordination (indoline or 2H-chromene fragment) is most preferable?
- How does coordination affect the thermal and photochromic properties of spiropyran?

Results and discussion

Performed calculations of spiropyran (2)–(4) showed (see Table 1) that the ground state of all the considered molecules is the closed-form. This result is in good agreement with the available data on the structure of similar compounds [25, 26]. The most stable isomer with the opened spirocycle is the structure *ttt*, which in spiropyran (2) ($R_1 = NO_2$, $R_2 = H$) is destabilized by 6.2 kcal/mol. Replacing the electron acceptor nitrogen-containing group with *o*-hydroxyaldehyde fragment increases the energy difference by about 1 kcal/mol. The predicted additional stabilization of the closed-form may indicate a shift of photoinhibited equilibrium toward this structure. The next in energy are *ctt* isomers, and structures corresponding to the *cis* form of spiropyran are the least preferred.

Spiropyran (2) could replace the benzoic acid residue in only one way—by coordinating the deprotonated carboxyl group to two zirconium ions. As in the isolated molecule, complex (1), $R_1 = NO_2$, $R_2 = H$ (consisting of (2) and UiO-67) will stabilize with a closed spirocycle form, which potentially ensures the preservation of the photochromic properties of the organic molecule.

Analysis of relative energies of the isomers of the compound discussed (Table 2) indicates significant reducing the energy gap between the ring-closed and the most stable ring-open *ttt* forms. This finding allows us to expect the facilitation of photo-transformations in the proposed complex (1), $R_1 = NO_2$, $R_2 = H$, as compared with the isolated spiropyran molecule. In order to estimate the stability of the formed compound, its stabilization energy is calculated relative to the dissociation into the initial components. According to the computational results, the target complex is by 1.9 kcal/mol more stable than model molecule UiO-67 and spiropyran (2). Therefore, the immobilization process of the original MOF with spirocyclic compound (2) is thermodynamically preferable, as it will lead to lowering the total energy of the system. It should be noted that the low stability of the formed complex may create difficulties in carrying out the corresponding experiments on obtaining modified UiO-67.

When studying complex (1), $R_1 = CHO$, $R_2 = OH$ with spiropyran (3) comprising *ortho*-located formyl and hydroxyl groups in the positions 6' and 7' of 2H-chromene fragment,

Table 1 The total (E_{total} , a.u.) and relative (ΔE , kcal/mol) energies of spiropyran (2)–(4) calculated by the DFT B3LYP/Def2-TZVP method

	(2), $R_1 = NO_2$, $R_2 = H$		(3), $R_1 = CHO$, $R_2 = OH$		(4), $R_1 = COOH$, $R_2 = H$	
	E_{total}	ΔE	E_{total}	ΔE	E_{total}	ΔE
<i>close</i>	−1259.00130	0.0	−1243.05188	0.0	−1243.06958	0.0
<i>cis</i>	−1258.98284	11.6	−1243.03271	12.0	−1243.04925	12.8
<i>cis-trans-trans (ctt)</i>	−1258.98920	7.6	−1243.03844	8.4	−1243.05614	8.4
<i>trans-trans-trans (ttt)</i>	−1258.99146	6.2	−1243.04049	7.1	−1243.05843	7.0

Table 2 The total (E_{total} , a.u.), relative (ΔE , kcal/mol), and stabilization (E_{stab} , kcal/mol) energies of the isomers of complexes (1), ($R_1 = \text{NO}_2$, $R_2 = \text{H}$, CHO , COOH) of UiO-67 modified with spiropyrans (2)–(4) calculated by the DFT B3LYP/Def2-TZVP method

	(1), $R_1 = \text{NO}_2$, $R_2 = \text{H}$		(1), $R_1 = \text{CHO}$, $R_2 = \text{OH}$		(1), $R_1 = \text{COOH}$, $R_2 = \text{H}$	
	E_{total}	ΔE	E_{total}	ΔE	E_{total}	ΔE
<i>close</i>	-6768.77868	0.0	-6752.82970	0.0	-6752.84794	0.0
<i>close_alt</i>	-	-	-6752.82127	5.3	-6752.84601	1.2
<i>cis</i>	-6768.76233	10.3	-6752.81283	10.6	-6752.83085	10.7
<i>cis_alt</i>	-	-	-6752.79621	21.0	-6752.83303	9.4
<i>ctt</i>	-6768.76975	5.6	-6752.81965	6.3	-6752.83723	6.7
<i>ctt_alt</i>	-	-	-6752.80588	15.0	-6752.83753	6.5
<i>ttt</i>	-6768.77187	4.3	-6752.82155	5.1	-6752.84095	4.4
<i>ttt_alt</i>	-	-	-6752.80808	13.6	-6752.84220	3.6
E_{stab}^*	-	-1.9	-	-2.1	-	-2.5

*Stabilization energy was calculated by means of subtraction of the sum of the energies of the complex (1) and benzoic acid from the sum of the energies of the unsubstituted UiO-67 and the corresponding spiropyran in ring-closed form

two ways of substitution of benzoic acid have been investigated, the first of which is analogous to that described above (coordination by carboxyl group). The second way (*alt*) implies interaction by means of *o*-hydroxyaldehyde group, which forms with two zirconium ions potentially less strained six-membered cycle. The latter may be the reason for the preference of such type complexation. However, the significant distances between the zirconium and oxygen atoms in structures (1), $R_1 = \text{CHO}$, $R_2 = \text{OH}$ *close_alt* and (1), $R_1 = \text{CHO}$, $R_2 = \text{OH}$ *ttt_alt* caused by steric hindrances (Fig. 2) point to the low probability of realization of the discussed route.

This assumption is confirmed by the results of the calculation of relative energies of the isomers comprising the same

forms of spiropyran coordinated by carboxyl or *o*-hydroxyaldehyde fragments. As follows from the data collected in Table 2, coordination on the first route leads to the formations of the structures with ring-closed spiropyran, which is by 5.3 kcal/mol energy preferred than isomer found for the alternative way of attaching spiropyran. Analysis of the relative energies of the isomers with merocyanine forms indicates the presence of an even more significant energy difference, reaching up to 10 kcal/mol. Destabilization of the most stable isomer relative to the isolated molecules of UiO-67 and (3) by 3.2 kcal/mol witnesses thermodynamically instability of the complex (1), $R_1 = \text{CHO}$, $R_2 = \text{OH}$ with coordinated spiropyran by means of *o*-hydroxyaldehyde group. At the

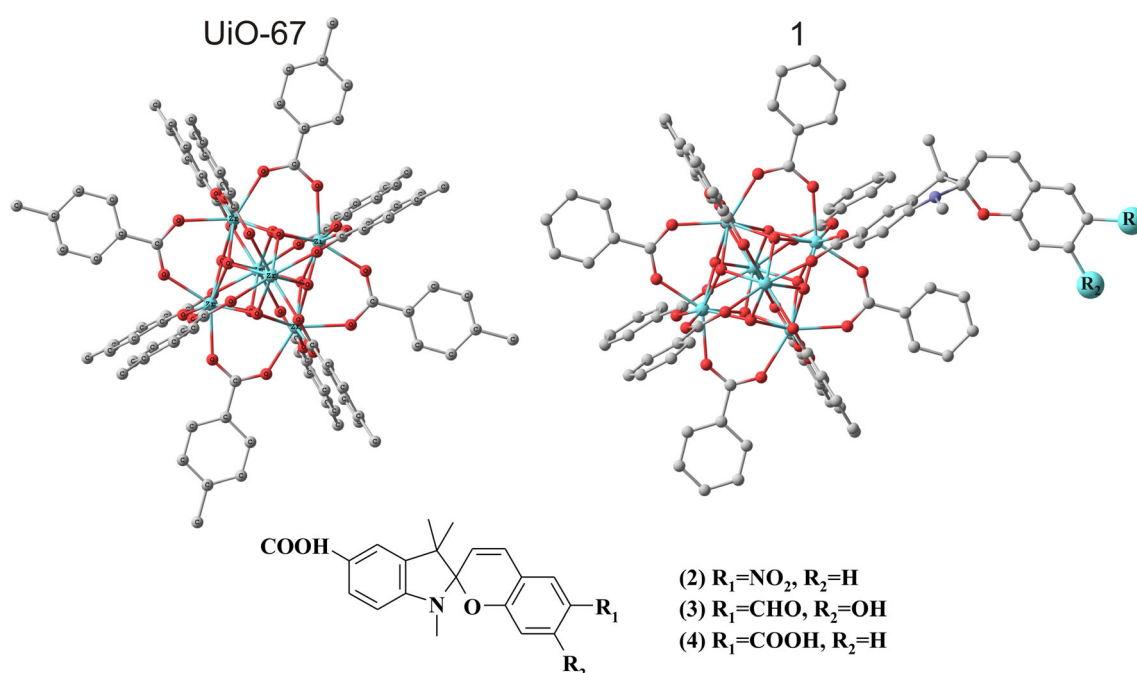


Fig. 1 Model MOF, complex (1), and spiropyrans (2)–(4). Hydrogen atoms are omitted for clarity

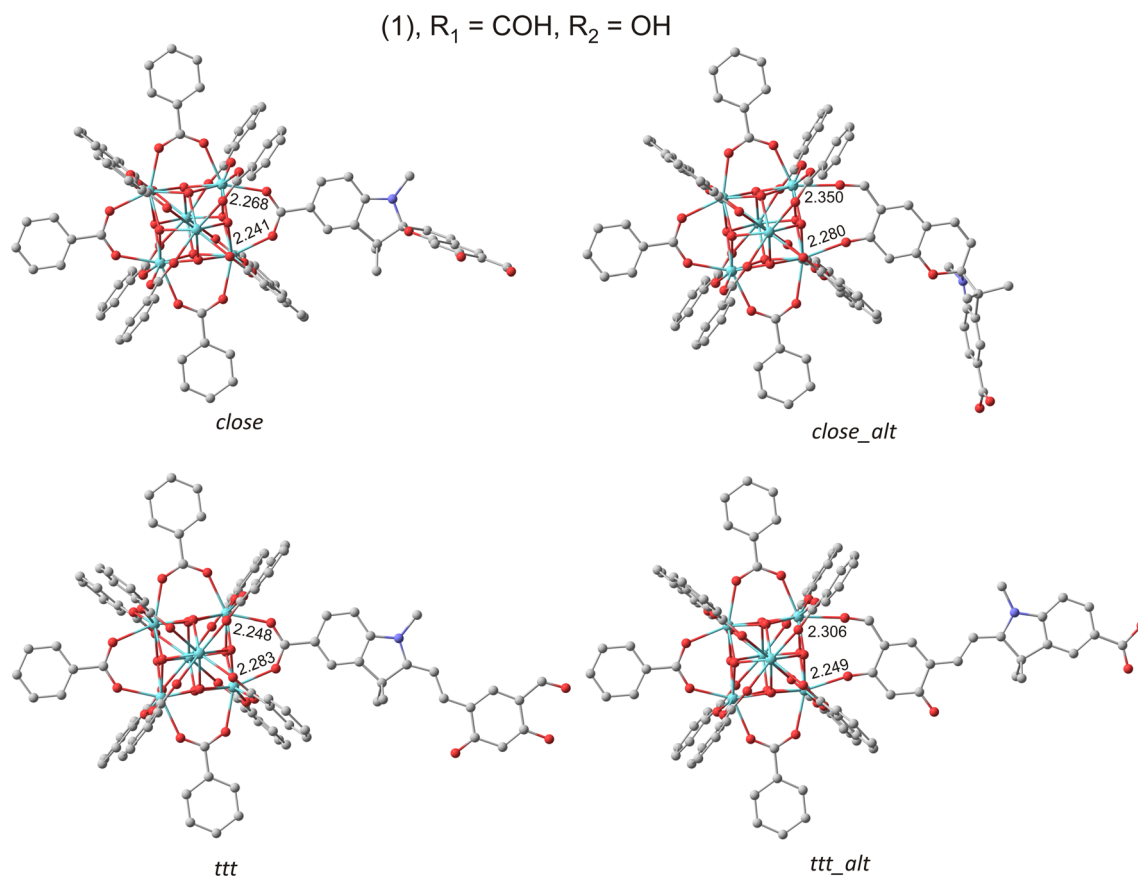


Fig. 2 Spatial structure of the isomers of the complex (1), $R_1 = \text{CHO}$, $R_2 = \text{OH}$ with different coordination of spiroyrans. Hydrogen atoms are omitted for clarity

same time, coordination of (3) with carboxyl group results on the energy preference of the complex (1), $R_1 = \text{CHO}$, $R_2 = \text{OH}$ by 2.1 kcal/mol relative to the initial components.

The last system to be considered as (1) is spiropyran with carboxyl groups ($R_1 = \text{COOH}$, $R_2 = \text{H}$) in the indoline and pyran cycles. Identical stereochemistry of coordinating moieties gives reasons to expect the manifestation of ambidentate properties by (4) and also the possibility of substitution of the 4,4'-biphenyldicarboxylic acid molecules between to two sites of UiO-67 under certain conditions. As in the complex (1), $R_1 = \text{CHO}$, $R_2 = \text{OH}$, structure with the ring-closed form of spiropyran coordinated by indoline moiety corresponds to the most stable isomer (Table 2). This isomer is by 4 kcal/mol preferred relative to the ring-open *tnt*-merocyanine. The stabilization energy of the compound discussed is equal to 2.5 kcal/mol, which is slightly higher than the value predicted for the complex (1), $R_1 = \text{CHO}$, $R_2 = \text{OH}$. At the same time, the calculation of the complex (1), $R_1 = \text{COOH}$, $R_2 = \text{H}$ with organic photochrome (4) coordinated by pyran moiety leads to the structure destabilized by 1.2 kcal/mol. This magnitude not exceeding stabilization energy allows us to expect the realization of alternative ways of immobilization of UiO-67 by spiropyran (4) and also gives reasons to suppose the possibility of substitution of linker biphenylcarboxylic groups between zirconium fragments by photochrome (4).

Conclusions

To sum up, by means of large-scale computer modeling with the use of density functional theory method in B3LYP/Def2-TZVP approximation, complexation of the model of MOF UiO-67 with various spiroyrans comprising donor groups containing oxygen atoms has been studied. The possibility of the formation of such mixed-ligand complexes is shown. The decrease in the energy difference between the ring-closed and merocyanine forms of spiropyran when coordination allows expecting the preservation of the photochromic properties of the organic molecules, which opens up prospects for the use of MOF modified in this way as photoactive sensors. Regardless of the substituents in the 2H-chromene part of spiropyran, the most preferred way of immobilization of UiO-67 is the interaction with the carboxyl group in the indoline fragment. The fundamental differences of this approach to imparting MOF of photosensor properties from the previously used [23] are the possibility of immobilization of a large number of molecules, which will favor lowering the determined threshold, and strong chemical binding, providing for greater cyclicality of chemical sensor built on the basis of this type of organometallic systems.

Computational details

Quantum-chemical calculations were performed using the Gaussian 09 program package [27] by means of density functional theory (DFT) [28] with B3LYP/Def2-TZVP approximation [29, 30]. The stationary points on the potential energy surfaces (PESs) were located by full geometry optimization with the calculation of force constant matrices and checked for the stabilities of DFT wave function. Geometry optimization has been performed without symmetry constraints and freezing individual atoms. All the calculations are carried out in vacuum without taking into account for the non-specific solvation, since we were interested in the MOF's properties in solid state. Graphical visualizations of the molecular structures presented in Figs. 1 and 2 were prepared using the ChemCraft software [31].

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