

Photoswitching molecules functionalized with optical cycling centers provide a novel platform for studying chemical transformations in ultracold molecules

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A novel molecular structure that merges the fields of molecular optical cycling with molecular photoswitching is presented. It is based on a photoswitching molecule azobenzene functionalized with one and two CaO- groups, which can act as optical cycling centers (OCCs). This paper characterizes the electronic structure of the resulting model systems, focusing on three questions: (1) how the electronic states of the photoswitch are impacted by a functionalization with an OCC; (2) how the states of the OCC are impacted by the scaffold of the photoswitch; (3) whether the OCC can serve as spectroscopic probe of isomerization. The experimental feasibility of the proposed design and the advantages that organic synthesis can offer in further functionalization of the molecular scaffold are also discussed. This work brings into the field of molecular optical cycling a new dimension of chemical complexity, intrinsic only to polyatomic molecules.

I. INTRODUCTION

The CaO- group attached to a molecular scaffold can function as an optical cycling center (OCC). Molecules functionalized with OCCs can be laser-cooled by scattering thousands of photons with a minimal loss of the population from the cycling pair of states (preferably, the ground state and the lowest excited state). Laser-cooled molecules are exploited in quantum technologies as well as in studies of fundamental physical phenomena^{1–16} and ultracold chemistry^{17–29}. The idea of using OCCs in polyatomic molecules builds on the success of laser-cooling of diatomic molecules^{30–42}. The electronic structure of laser-cooled molecules (all the way through hyperfine structure), their applications, and recent experimental advances are thoroughly covered in recent reviews^{43–49}.

The CaO- group can function as an OCC because it supplies the molecule with an access to an electronically excited state that spontaneously decays almost exclusively to the molecular (electronic and vibrational) ground state^{50–57}. Other quantum functional groups suitable for laser cooling, such as SrO- and YbO-, have also been identified^{57–87}.

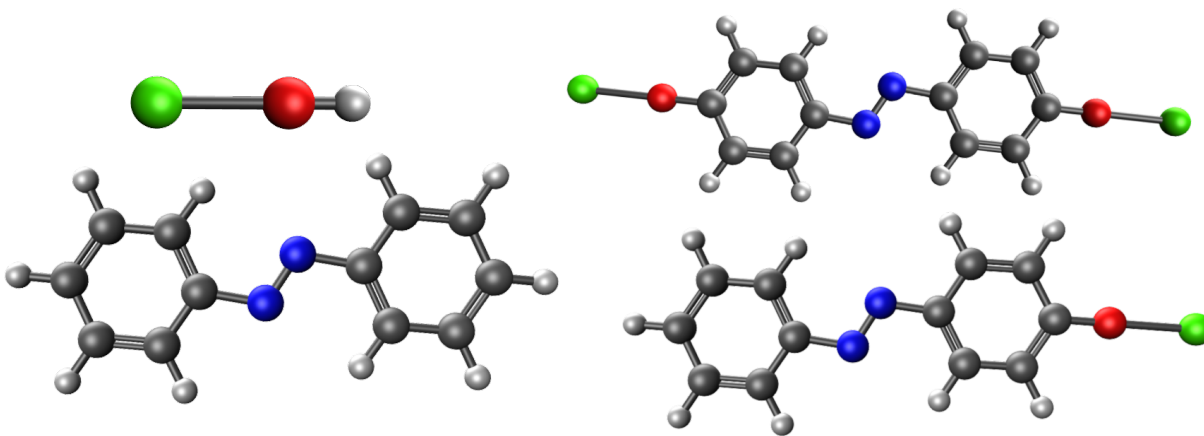


FIG. 1: Molecules studied in this work. Counterclockwise from the left top: CaOH, azobenzene (AB), para-CaO-azobenzene (pAB), and bis-(para-CaO)-azobenzene (bpAB).

One—thus far only hypothesized but exciting—possibility is to use quantum functional groups, such as CaO- OCCs, for precise optical sensing of chemical events. For example, it would be desirable to have an optical reporter that can detect a chemical change, such as a conformational change or a chemical reaction, in a part of the molecule distant from the reporter. Because OCCs are electronically isolated from the rest of the molecule by

design, it might appear as a contradiction that an OCC can be used for such a sensing. However, OCCs rely on transitions with narrow linewidths, which may feature small but detectable shifts and exhibit other delicate effects such as Fermi resonances arising from accidental degeneracies of vibrational states⁸³, all of which may serve as an optical signature of chemical reactions.

As a model reaction to investigate this concept, we have chosen photoisomerization of azobenzene (AB)^{88,89} (shown in Fig. 1). The photoisomerization of AB from the more stable *trans*-conformation to the less stable *cis*-conformation is triggered by the ultraviolet light of the 300-400 nm wavelength (3.1-4.1 eV)^{90,91}, which is different from the OCC transition (about 650 nm or 1.9 eV). Thus, it should be possible to excite the respective transitions independently. In the dark, the *cis*-isomer has a substantial lifetime, slowly relaxing back the *trans*-isomer at room temperature. We hypothesize that an OCC located far from the azo bridge can optically report on photoisomerization—a model chemical event that is relatively easy to probe in the gas phase.

Furthermore, controlling the OCC separation and dipole alignment through a chemical or physical handle (such as photoswitching) brings an interesting new dimension into quantum information science (QIS). For this reason, we also study azobenzene decorated with two CaO- OCCs located one on each of the two benzene rings. The possibility of chemical sensing with OCCs and controlling the spatial arrangement of multiple OCCs by means of an “orthogonal” chemical transformation are both of fundamental importance and of interest to the field of QIS.

In this contribution we investigate the electronic structure of molecules comprising the CaO- and azobenzene (AB) moieties: para-CaO-azobenzene (pAB) and bis-(para-CaO)-azobenzene (bpAB); the relevant structures are shown in Fig. 1. The electronic states of pAB are of three types: the electronic states similar to these of the scaffold (AB-like), the electronic states localized on the OCC (OCC-like), and the electronic states of a mixed character.

The quantum-chemical description of such systems is far from trivial, owing to their open-shell character^{52,86,87}. We use methods from the equation-of-motion coupled-cluster (EOM-CC) family to describe relevant electronic states of these molecules. EOM-CC provides a robust and versatile approach to electronically excited and open-shell species^{92–95}. As shown in Fig. 2, different variants of EOM-CC provide access to different types of states. Molecules

with a single unpaired electron (CaOH, pAB) are well described by EOM-EA-CC (EOM-CC for electron attachment). EOM-EE-CC (EOM-CC for excitation energies) describes excited states of closed shell molecules (AB), but it can also be used for open-shell species such as pAB. EOM-DEA-CC (EOM-CC for double electron attachment) and EOM-SF-CC (EOM-CC with spin-flipping excitations) are the preferred methods for diradicals (bpAB)^{96,97}.

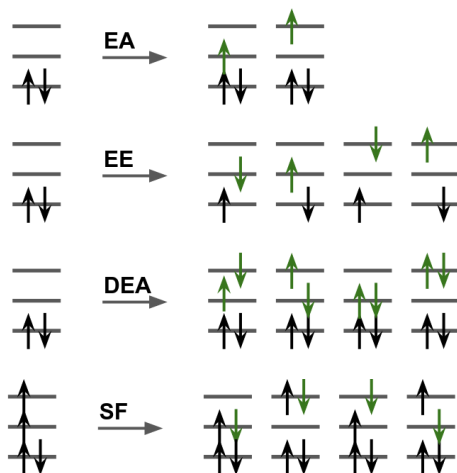


FIG. 2: EOM-CC models used in this work. Color illustrates the action of the EOM operator (only single excitations are shown). An EOM method is defined by specifying the reference determinant and the type of generalized excitation operator—e.g., spin and electron-conserving operators are used in EOM-EE, spin-flipping operators are used in EOM-SF, and non-particle conserving operators are used in EOM-EA and EOM-DEA.

The paper is organized as follows. The next section provides details about the computational approach. In section III we review the electronic structure of the prototype moieties (AB, Ca-OH) and then characterize the electronic states of the pAB and bpAB. We focus on the three questions: (1) How the states of the scaffold are impacted by the OCC? (2) How the states of the OCC are impacted by the scaffold? (3) Can we employ the OCC as a spectroscopic probe of the isomerization reaction? We then discuss preliminary results of the synthetic efforts and outline future directions.

II. THEORETICAL METHODS AND COMPUTATIONAL DETAILS

We use methods from the EOM-CC family^{92–95}, which employ the following ansatz

$$\Psi = Re^T\Phi_0, \quad (1)$$

where Φ_0 is the Hartree–Fock (HF) reference determinant and T is the cluster operator

$$T = \sum_{ia} t_i^a a^\dagger_i + \frac{1}{2!^2} \sum_{ijab} t_{ij}^{ab} a^\dagger_i b^\dagger_j + \dots, \quad (2)$$

where the operators, $a^\dagger, b^\dagger, i, j$ are the fermionic creation and annihilation operators adding or removing electrons to molecular orbitals $\varphi_a, \varphi_b, \varphi_i, \varphi_j$. The choice of reference Φ_0 determines the separation between the occupied and virtual spaces⁹⁸. The amplitudes t are found by solving the coupled-cluster equations obtained by projecting the similarity transformed Schrödinger equation

$$\exp(-T)H\exp(T)\Phi_0 = E_{CC}\Phi_0 \quad (3)$$

onto the space spanned by the reference determinant Φ_0 , all singly $\{\Phi_i^a\}$, doubly $\{\Phi_{ij}^{ab}\}, \dots$ substituted determinants. In this work we use EOM-CC models with the expansion truncated after the second term, EOM-CC with single and double substitutions (EOM-CCSD).

The EOM operator, R , has the form that depends on a particular flavor of EOM (as illustrated in Fig. 2). We use EOM-CC methods that are best suited for each type of electronic states studied here

- EOM-EA-CCSD^{99–101}. In this method the Hartree–Fock reference corresponds to a closed-shell cation and the EOM operator R has one more creation than annihilation operators, giving rise to the EOM-EA-CCSD wave-functions of the neutral states. This method is suitable for CaOH and pAB.
- EOM-EE-CCSD.¹⁰² The EOM-EE excitation operator preserves the number of electrons and generates electronically excited states⁹³. For the closed-shell references, the excited states are naturally spin-adapted, forming singlet or triplet excitations. EOM-EE-CCSD can also be applied to open-shell references although in this the wavefunctions might be slightly or severely spin-contaminated^{92,103,104}, depending on the type of an excitation. This method is suitable for AB and to pAB, with the caveats discussed below.

- EOM-SF-CCSD^{97,105–108}. The EOM-SF operator preserves the number of electrons, but flips the spin of one electron. This method uses a high-spin ($M_s = 1$) triplet state as a reference and describes the singlet and the low-spin ($M_s = 0$) components of the triplet states. The description of the higher-lying states is not accurate due to spin-incompleteness.
- EOM-DEA-CCSD^{96,100,109,110}. The EOM-DEA operator increases the number of electrons by two. The Hartree–Fock reference for this method is a closed-shell dication. This method is suitable for bpAB; it can describe both the diradical states as well as higher excited states, which was exploited in previous studies of molecules with two OCCs (bi-OCCs)^{26,86,87}.

Below we provide more details about computational protocols employed.

Computational protocols

We described the electronic states of azobenzene functionalized with a single OCC using the EOM-EA-CCSD method. We also used this method to optimize the structure of the molecule in its ground electronic state. We then used this method to compute the low-lying excited states at the optimized geometry. We note that EOM-EA-CCSD can only accurately describe states dominated by the OCC transitions because states involving molecular orbitals of the scaffold will appear as $2p1h$ (two-particle-one-hole) excitations. To gain access to these states, we calculated excited states with EOM-EE-CCSD starting from an open-shell doublet reference.

We described the azobenzene molecule functionalized with two OCCs with the same methodology as in our previous work on bi-OCCs^{26,86,87}. We optimized geometry of the ground electronic state with EOM-SF-CCSD¹⁰⁶ and computed the excitation energies at the optimized geometry with the EOM-DEA-CCSD method.

We used Dunning’s cc-pVDZ basis set for geometry optimization and aug-cc-pVDZ for excitation energies^{111–113}. All CC and EOM-CC calculations were carried out with *Q-Chem*^{114,115}. Orbitals and structures were visualized with the *IQmol* and *Jmol* molecular visualization tools^{116,117}.

In the supplemental information (SI), we provide Cartesian coordinates of relevant structures, Franck-Condon factors for the cycling transitions, as well as benchmark calculations with time-dependent density functional theory.

Wavefunction analysis

We analyzed transitions between the electronic states using a compact representation of the transitions between the two many-body states by means the natural transition orbitals (NTOs)¹¹⁸. NTOs are defined as the left and right singular vectors of the one-particle transition density matrix^{119–121}:

$$\gamma_{pq}^{f \leftarrow i} = \langle \Psi_f | p^\dagger q | \Psi_i \rangle, \quad (4)$$

where Ψ_i and Ψ_f are the two states involved in the transition. $\gamma_{pq}^{f \leftarrow i}$ is related to one-particle transition density, $\rho^{f \leftarrow i}(r_h, r_p)$,

$$\begin{aligned} \rho^{f \leftarrow i}(r_h, r_p) &= N \int \Psi_i(r_h, r_2, \dots, r_n) \Psi_f(r_p, r_2, \dots, r_n) dr_2 \dots dr_n \\ &= \sum_{pq} \gamma_{pq}^{f \leftarrow i} \varphi_p(r_h) \varphi_q(r_p), \end{aligned} \quad (5)$$

where N is the number of electrons.

Visual inspection of the NTOs enables characterization of the electronic states. However insightful, such analysis can be tedious and somewhat subjective. The wavefunction analysis tools afford direct extraction of information about the character of the wavefunction. We use the *TheoDORE* package to automate this analysis¹²². In particular, we are interested in the extent of charge transfer between the scaffold and OCCs, which can be used to quantify the extent of electronic coupling between the two moieties. Charge-transfer numbers (CTNs) is an exciton descriptor, which provides a measure of charge transfer between different parts of the system. The partition of electrons between fragments A and B is given by integrating the $\gamma^{f \leftarrow i}$ over restricted regions

$$\Omega_{AB} = \int_A dr_h \int_B dr_p |\gamma(r_h, r_p)|^2. \quad (6)$$

Thus, CTNs can be interpreted as the number of electrons transferred between A and B . In these calculations, the only user-required input is a partition of the molecule into fragments¹²². This analysis depends on the definition of the region boundaries, similarly to the Mulliken charges.

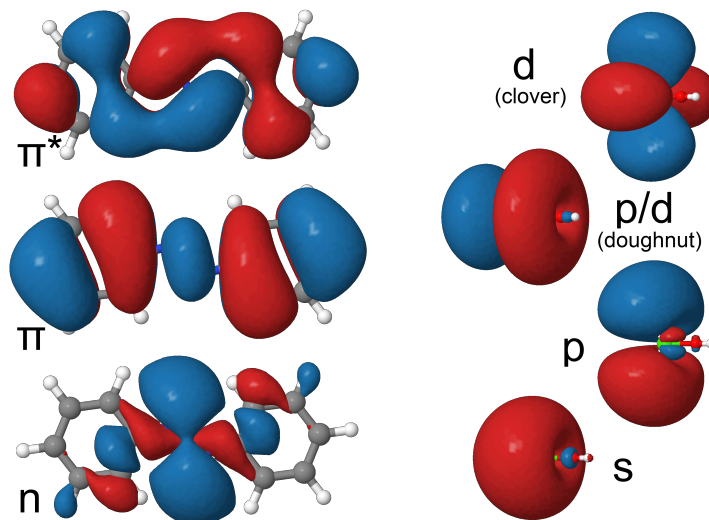


FIG. 3: NTOs of the relevant electronic transitions in the *trans*-AB (left) and CaOH (right).

III. RESULTS AND DISCUSSION

A. Electronic structure of AB and CaOH

We begin by reviewing the electronic states of AB and CaOH. Fig. 3 shows relevant molecular orbitals (MOs).

The ground state of AB is a closed-shell singlet. The excited states of AB are derived by promotion of an electron from the nitrogen (azo) bridge (relevant MOs are π and lone-pair n ; see Fig. 3). The first excited singlet state is a dark $n\pi^*$ transition. The second excited singlet state is a bright $\pi\pi^*$ transition. At the EOM-EE-CCSD/aug-cc-pVDZ level of theory, the energies of these transitions are 3.055 eV and 4.465 eV, respectively. In both states, electrons of the nitrogen bridge MOs are promoted to an antibonding orbital, effectively weakening the double bond and lowering the barrier along the *cis-trans* rotation coordinate. Below, we refer to the excited states generated by transitions localized on the AB scaffold as the AB-like states, or the scaffold-like states.

Next, we review the electronic states of CaOH, which can be described as a hydrogen-terminated OCC. Extensive spectroscopic data is available for this molecule^{123–130}. CaOH is one of a few polyatomic molecules that have been laser-cooled, paving the way for advanced quantum-state control experiments^{131–137}. CaOH is a doublet radical with one unpaired

electron localized on the metal. The low-lying electronic states of CaOH resemble the states of an alkali atom (Fig. 3). Both the ground and the low-lying excited electronic states can be described as a closed-shell core with a single valence electron occupying hydrogen-atom-like orbitals. In the ground state (X state), the unpaired electron is localized on the Ca atom, resembling the ^2S atomic state. The first pair of excited states (A and B states) are ^2P -like states, with degeneracy lifted in non-linear structures. The $\text{X} \rightarrow \text{A}$ transition energy for CaOH is around 2 eV. Higher CaOH states also follow this pattern of a localized atomic-like transitions of a single unpaired electron. Below we refer to these states as OCC-like states. This type of states is commonly found in molecules functionalized with the CaO-group^{57,79,131,138}.

B. Electronic states of pAB

The electronic states of pAB can be classified as either AB-like, OCC-like, or as states of a mixed character. The key question is the extent to which the AB-like and OCC-like states perturb each other. Previously, the effect of the electronic states of the scaffold on the OCC-like states was explored by Dickerson and coworkers^{77,78}. They found that when the energy of the first excited state in the unfunctionalized scaffold comes close to the energy of the cycling transition, the two electronic states begin to interact, spoiling the localized character of the OCC transitions. Here we apply similar analysis to electronic states of functionalized AB.

We begin exploring an interplay between the OCC and AB moieties by inspecting the electronic states of a singly functionalized molecule, pAB model system in which the CaO-group is located at the *para* position with respect to the nitrogen bridge (see Fig. 1). Placing the CaO- group in the *para* position minimizes the steric repulsion, which is favorable for laser cooling⁷⁹.

The electronic states of pAB, the molecule comprising the CaOH and AB moieties, can be correlated to the states of its building blocks. Similar to other molecules functionalized with CaO- groups, the low-lying states of *trans*-pAB are clearly identifiable as OCC-like. The first state with a non-OCC features appears at 3.5 eV as the 6th excited doublet state. This state derives from a π^* orbital on the azo bridge with a *p/d* admixture on the metal. The transition to this state differs from the $\text{S}_0 \rightarrow \text{S}_1$ transition of *trans*-AB as it does not

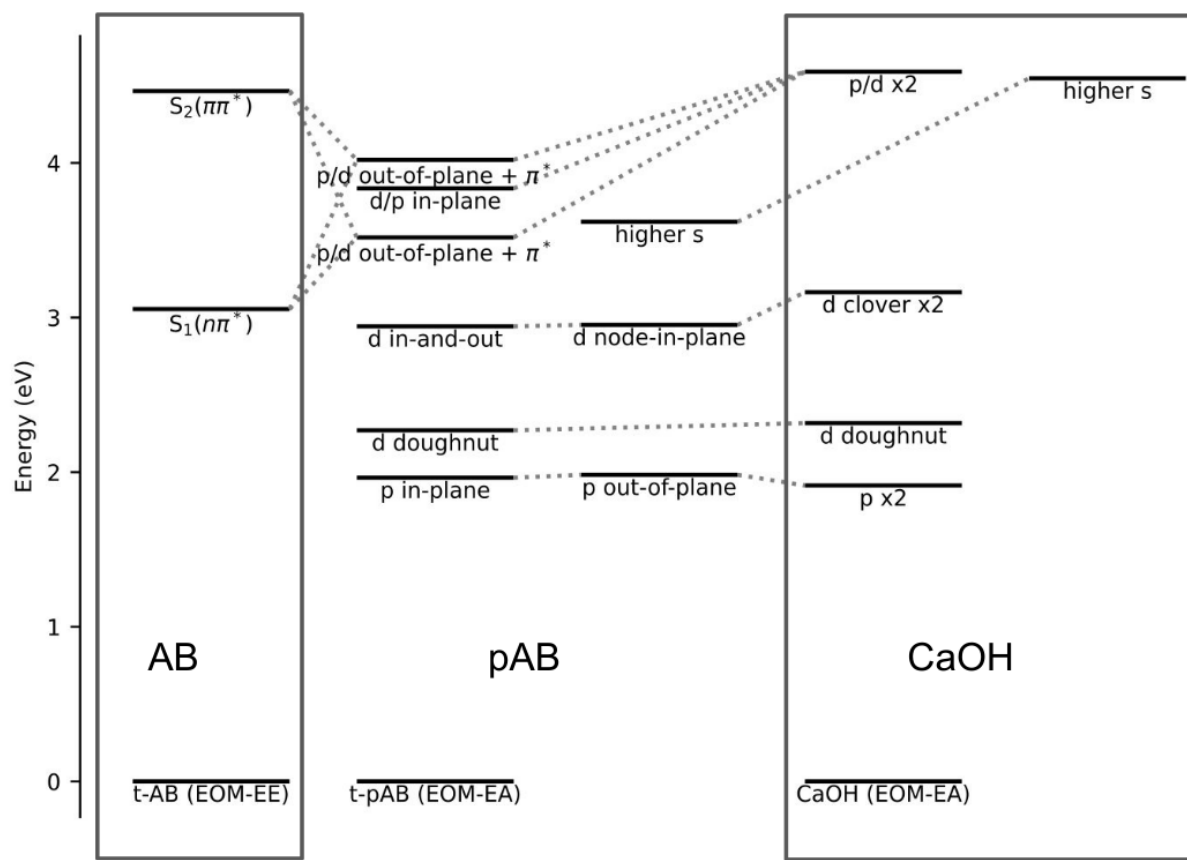


FIG. 4: Electronic states of *trans*-pAB (central panel; EOM-EA-CCSD/aug-cc-pVDZ at EOM-EA-CCSD/cc-pVDZ geometry) as a combination of *trans*-AB states (the column on the left; EOM-EE-CCSD/aug-cc-pVDZ at CCSD/cc-pVDZ geometry) and the OCC states (CaOH; two columns on the right EOM-EA-CCSD/aug-cc-pVDZ at a EOM-EA-CCSD/cc-pVDZ geometry). Energies of the respective ground states are set to zero.

originate from a promotion of a lone-pair n to the π^* orbital, but rather it is the s -type orbital of the OCC which is excited. Interestingly, the next two states recover the OCC-like character and can be identified as s -like and p/d -like. The 9th excited state located vertically at 4.0 eV is of a mixed character.

Fig. 4 summarizes the electronic states of *trans*-pAB. The states of an OCC-like character are preserved for excitation energies below the first excited state of the unfunctionalized AB, but some of the OCC-like states are present also above this threshold. The states of a mixed character appear close and above this threshold.

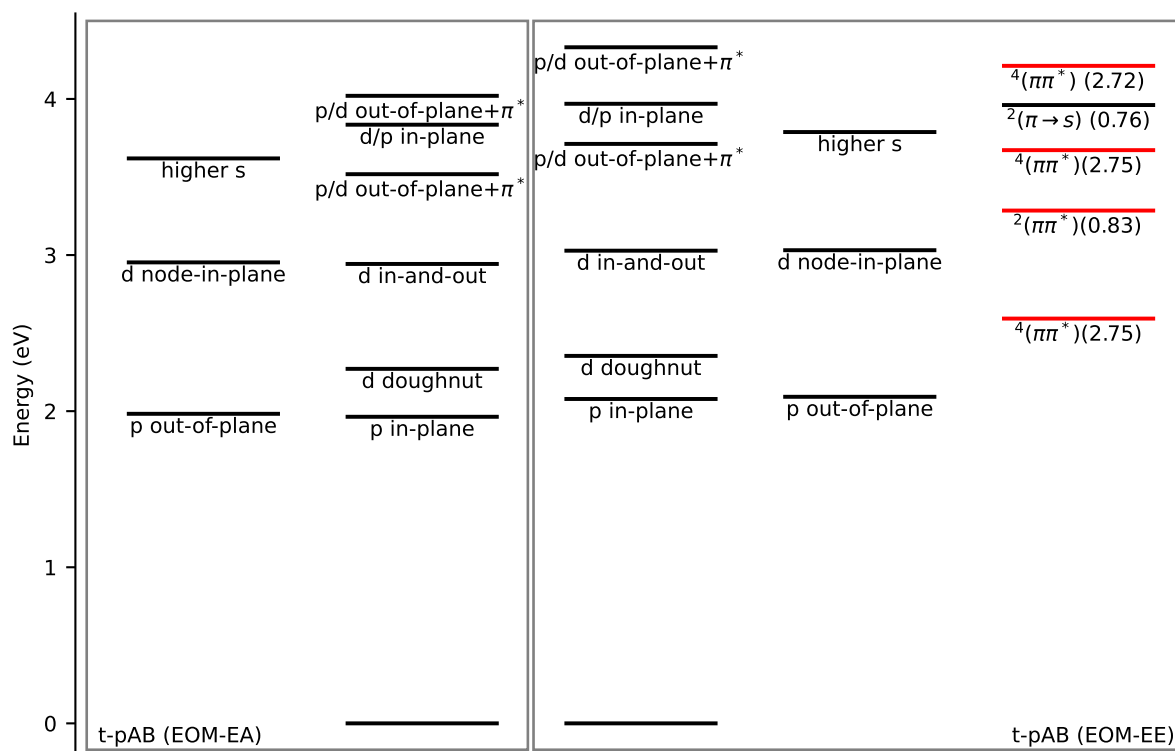


FIG. 5: *Trans*-pAB at the EOM-EA-CCSD/cc-pVDZ geometry. Comparison of the EOM-EA-CCSD/aug-cc-pVDZ states (two columns on the left) with the states computed with EOM-EE-CCSD/aug-cc-pVDZ (three columns on the right). The rightmost column shows the EOM-EE-CCSD states absent in the EOM-EA-CCSD calculations; some of these extra states are spin-contaminated (red color); the corresponding values of $\langle S^2 \rangle$ are given in the parentheses.

As explained in the methods section, different flavors of EOM-CCSD are suitable for different types of states. In the case of pAB, we expect that EOM-EA-CCSD describes well the transitions localized on the OCC, but will give less accurate results for the transitions involving the scaffold orbitals. To gain a better handle on these states, we employ EOM-EE-CCSD. We also present wavefunction analysis of the resulting states.

The method of choice for the treatment of the excited states of AB is EOM-EE, however, using this method for the pAB molecule is complicated by its open-shell character,

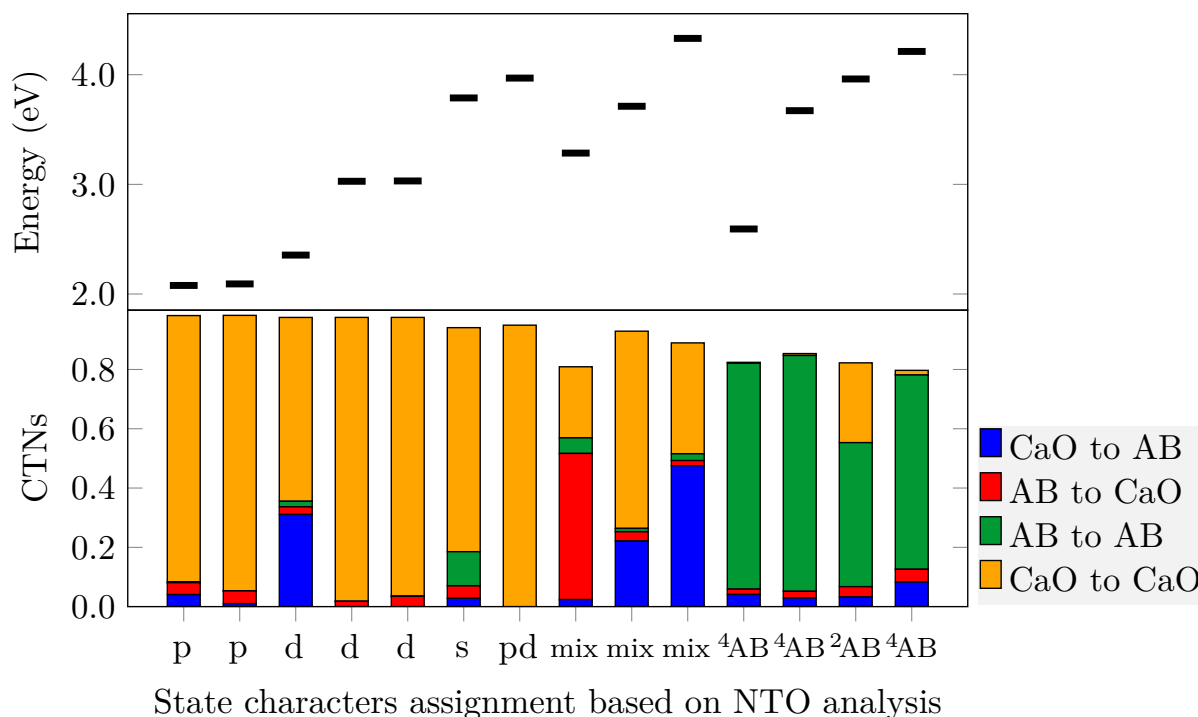


FIG. 6: Electronic states of *trans*-pAB and the character of the underlying wavefunctions. Top: state energies (relative to the ground state). Bottom: CTNs characterizing the transitions from the ground state. From left to right the states are ordered to match three groups: first are the OCC-like states (labeled *s*, *p*, and *d*), second are the states of a mixed character (*mix*), and the last are the AB-like states (labeled ^{2S+1}AB). Compare with Fig. 5. EOM-EE-CCSD/aug-cc-pVDZ at EOM-EA-CCSD/cc-pVDZ ground state's geometry.

which can lead to small or severe spin-contamination^{92,103,104}. Generally, states derived by excitations to or from open-shell orbitals are well-behaved⁹² whereas the states derived by excitations from doubly occupied to unoccupied orbitals are poorly described because of the spin-incompleteness of the EOM-EE-CCSD ansatz (this problem can be remedied by including selected triple excitations¹³⁹).

In *trans*-pAB, the spin-contamination of the reference Hartree–Fock determinant is small; it is also rather small for the most EOM low-lying states (~ 0.002). The EOM-EE-CCSD method generates spectrum of *trans*-pAB that qualitatively agrees with the EOM-EA-CCSD one. The EOM-EE-CCSD excitation energies are higher by about 0.15 eV. The transition dipole moments agree within 30% with the EOM-EA-CCSD ones.

The EOM-EE-CCSD calculations also yield a set of states that do not have counterparts among the EOM-EA-CCSD states. As anticipated, the EOM-EE-CCSD method yields excited states derived by promoting electrons localized on the AB moiety. These states can be classified as AB-like states of $\pi \rightarrow \pi^*$ type. One of the new states should again be characterized as a state of a mixed character as it derives from the $\pi \rightarrow s(\text{Ca})$ transition. Some of the AB-like states (especially quartets) show high spin-contamination, which indicates that their proper description would require inclusion of higher terms in the EOM-CC expansion (see Fig. 25 and the corresponding discussion in Ref. 92). Fig. 5 highlights the differences between EOM-EA-CCSD and EOM-EE-CCSD results.

Having described this manifold of excited states, we conclude this section by presenting the CTN-based analysis of their corresponding wavefunctions (pAB is partitioned into CaO and the rest). Here, CTNs can be interpreted as the number of electrons transferred between the OCC and AB moieties—perfectly decoupled localized transitions can be identified by zero CTNs. Fig. 6 shows the CTNs and the state energies. We highlight the following observations:

- Among states classified as OCC-like, the transitions are indeed localized on the CaO-moiety.
- The main outlier is the state visually assigned as *d* (doughnut). Fig. 7 shows NTOs for that state. Although visually the state appears to be localized on the CaO- group, the CTNs analysis shows that a significant portion of the electronic density is ascribed to the AB fragment. A similar observation about the analogous $\text{B}^2\Sigma^+$ state of SrOH was made in the previous study, where a significant contribution to the state was attributed to hydrogen's *s* orbital⁵³.
- The sum of all CTNs gives the norm of the one particle transition density, $\|\gamma\|$. The difference, $1 - \|\gamma\|$, quantifies the multiply excited character of the state. Spin-contaminated states are all ranking the highest in this metric, confirming that higher excited configurations are needed for a proper description of these states.
- CTNs highlight that the states labeled as of a mixed character are formed by promoting the ground state's $s(\text{Ca})$ electron to an orbital delocalized over the CaO- and AB moieties, or the other way around.

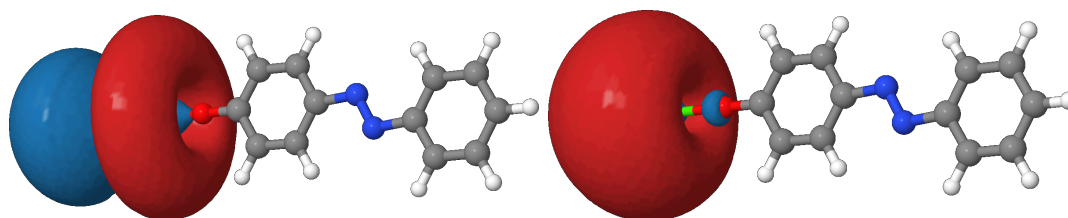


FIG. 7: Particle and hole NTOs for the $d(\text{Ca})$ (doughnut) state of *trans*-pAB. EOM-EE-CCSD/aug-cc-pVDZ at EOM-EA-CCSD/cc-pVDZ geometry of the ground state.

C. OCC as a spectroscopic probe to monitor isomerization

The key feature of azobenzene, which carries over to its functionalized versions, is its ability to assume two distinct geometries, the *cis*- and *trans*-isomers. Well known in photochemistry, this is a new element in the context of molecules functionalized with OCCs.

The distinct geometries of the two isomers of pAB make the two systems distinct, just as if the OCC were attached to two different scaffolds. The impact of scaffold on the properties of an OCC, which is of a central importance in the context of laser-cooling, have been extensively studied^{26,26,52,55,57,71,76–82,86,87}. Yet, the effect of the scaffold isomerization on the OCC states has not been investigated. Furthermore, what makes pAB special is that *cis*- and *trans*-isomers can be inter-converted. Such chemical complexity, which unique to polyatomic molecules, can bring a useful resource to QIS applications.

We now consider the other isomer of pAB, *cis*-pAB and compare the low-lying excited states of the two isomers, using the same computational protocol as above. The low-lying electronic states of *cis*-pAB are OCC-like. Table I highlights similarities of the $X \rightarrow A$ and $X \rightarrow B$ transitions in *trans*-pAB, *cis*-pAB and CaOH.

The key result of this calculation is the impact of the isomerization on the excitation energy of the cycling transition, $X \rightarrow A$. Although this value can be affected by a change of the ligand, the computed excitation energy change due to the isomerization is minute (on the order of 1 meV). Thus, pAB results show that AB acts, to a large extent, as an inert scaffold, carrying the OCC in space without impacting the characteristics of the cycling transition. This can be rationalized by the observation that in the gas-phase, the OCC does not experience large variations in its environment between the *trans*- and *cis*- isomers. Hence, one can imagine a scenario in which the inert AB scaffold can move the OCC to a

TABLE I: Excitation energies, eV, and oscillator strengths (in parentheses) of the *trans*-pAB, *cis*-pAB, and CaOH calculated with EOM-EA-CCSD/aug-cc-pVDZ at the EOM-EA-CCSD/cc-pVDZ geometries^a.

Transition	<i>trans</i> -pAB	<i>cis</i> -pAB	CaOH
X $\rightarrow$ A	1.964 (0.262)	1.964 (0.260)	1.915 (0.291)
X $\rightarrow$ B	1.983 (0.272)	1.980 (0.268)	1.915 (0.291)

^a EOM convergence thresholds set to 10^{-10} .

different local environment.

To create a situation when the environment of an OCC changes more drastically upon isomerization, we consider the AB scaffold with both phenyl rings functionalized in the *para* position with the CaO- moieties (bpAB), as shown in Fig. 8. In contrast to the isomerization of pAB, where the CaO- group did not sense large changes to its chemical environment, isomerization of bpAB changes the distance between two polar CaO- groups.

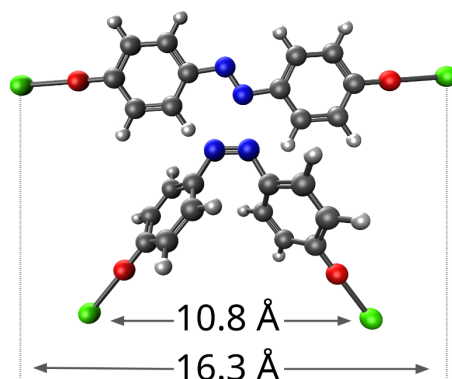


FIG. 8: The azobenzene molecule functionalized with two OCCs, bpAB. The isomerization reduces the distance between the two Ca atoms from 16.3 Å to 10.8 Å. Geometries optimized with EOM-SF-CCSD/cc-pVDZ.

The optimized geometries of the two isomers show that the structure of the CaO- moieties is preserved, meaning that the interactions between the two OCCs are weak and do not induce changes in the overall bonding pattern. The excitation energy from the ground state to the first excited state is shifted; this is an expected outcome related to the change in the electron withdrawing strength of the ligand.

The *trans*-to-*cis* isomerization reduces the distance between the two Ca atoms by almost one third of its initial value (see Fig. 8). Thus, we expect to observe a response to the isomerization in the OCCs optical properties. Table II shows the change in the excitation energy upon isomerization. In contrast to pAB, bpAB shows a much more appreciable change in the excitation energy.

TABLE II: Change in excitation energy (eV) of the $X \rightarrow A$ transition upon isomerization. Comparison between bare pAB and bpAB with an interacting group at both ends. Calculated with EOM-EA-CCSD/aug-cc-pVDZ (pAB) and EOM-DEA-CCSD/aug-cc-pVDZ (bpAB) at the geometry optimized as described in the methods section^a.

	pAB	bpAB
cis	1.964	1.968
trans	1.964	2.000
change	$\lesssim 0.001$	0.032

^a EOM convergence thresholds set to 10^{-10} .

D. Synthetic Efforts: Preliminary results and future work

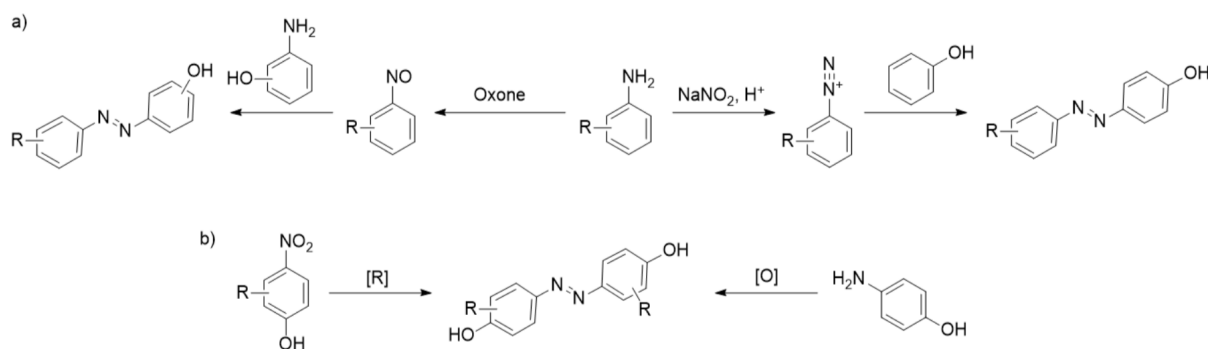


FIG. 9: (a) Synthetic routes for asymmetric azobenzene derivatives using Mills reaction (left) and diazotization method (right). (b) Synthetic routes for symmetric azobenzene derivatives.

CaO-azobenzene can be produced by reacting the precursor ligand 4-hydroxyazobenzene (*trans* form purchased from Sigma Aldrich) with metastable Ca atoms generated from laser

ablation in a cryogenic buffer gas cell, as previously discussed in the context of the production of CaOC_6H_4 molecules and their functionalized derivatives^{57,80,83}. However, initial experiments have revealed that the yellow powder of 4-hydroxyazobenzene undergoes a color change to black at $\sim 100^\circ\text{C}$, well below its melting point of 155°C . This suggests the thermal decomposition of azobenzene¹⁴⁰, making it unlikely to generate sufficient precursor vapors for the reaction. To address this issue, the precursor can be functionalized with electron-withdrawing groups, such as fluorine atoms, to enhance its thermal stability¹⁴⁰. Alternatively, a solid-phase method⁷⁹ can be adopted. A mixture of CaH_2 and precursor powder (1:1 molar ratio), with polyethylene glycol or silver powder as a binder, can be thoroughly mixed and ground before being pressed into a pellet for direct laser ablation. Preliminary results with the Sr-equivalent have shown two peaks in the excitation spectra. Further experiments of using CaH_2 and precursor to produce CaO-azobenzene will be performed. In addition, the precursor ligand only exists in the *trans* isomeric form, enabling photoswitching to the *cis* isomer upon laser illumination. Specifically, the precursor 4-hydroxybenzene has been reported to undergo photoswitching at $\sim 360\text{ nm}$ (3.44 eV)^{90,91}. A 360 nm UV LED or pulsed Nd:YAG laser at 355 nm (3.49 eV) can be employed to initiate the photoswitching process of CaO-azobenzene. To measure the branching ratios of the $X \rightarrow A$ and $X \rightarrow B$ transitions of these molecules, dispersed laser-induced fluorescence (DLIF) spectroscopy can be taken either with a pulsed dye laser used in the previous works^{80,83}, or with a continuous-wave (CW) dye laser which is currently under installation in our lab. The narrow line-width and the broad scanning range of the CW dye laser allow us to significantly suppress the background noise and enable us to obtain high-resolution spectra of these azobenzene molecules.

With many azobenzene derivatives commercially available, properties of the OCC-photoswitch system can be tuned using varying functionalizations. Several synthetic routes can access those derivatives that are not commercially available. A widely used synthetic route involves diazotizing an aromatic amine using sodium nitrite in the presence of strong acid to afford the resulting diazonium salt, which can then be coupled with phenol to give azobenzene product (Figure 9a).^{141,142} Alternatively, the Mills reaction can also be used where an aromatic amine is oxidized to a nitroso intermediate (Figure 9a). This species can then be reacted with a separate aromatic amine to yield the azobenzene. For symmetric azobenzenes (bi-OCCs), the desired product can be afforded through reductive coupling of aromatic nitro compounds using a reducing agent or oxidative coupling of aromatic amines

using an oxidizing agent to achieve the same transformation (Figure 9 b)^{141,142}.

IV. CONCLUSIONS AND OUTLOOK

We have presented a comprehensive study of electronically excited states in a model photoswitch molecule functionalized with one or two OCCs. The excited-state analysis shows how the atomic-like and scaffold-like character becomes mixed for excitation energies close and above the first excitation energy of the unfunctionalized scaffold. Using state-of-the-art *ab initio* methods, we have characterized the new type of states that arises from the mixing. The complete description of these states is challenging and use of higher order CC methods might be necessary not only to achieve high accuracy but also for qualitative agreement. Interestingly, we have found that the OCC-like states can exist even at energies above the energy of the first excited state of the scaffold.

Following the extensive characterization of the relevant electronic states, we have considered spectroscopic signatures of the scaffold’s isomerization. The calculations show that the OCC can witness and report on the isomerization process. The azobenzene’s scaffold allows the OCCs excitation energy to report on its changing environment. Functionalization of the azobenzene’s frame with a second OCC results in a model system in which the first OCC can experience anisotropy of the space through which the isomerization process takes it. Correlation between the excitation energy changes and the assumed isomer gives a spectroscopic probe for observation of the isomerization chemistry.

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Conflicts of interest

The authors declare the following competing financial interest(s): A.I.K. is the president and a part-owner of Q-Chem, Inc.

Supplementary Material

DFT benchmarks; Franck-Condon factors; Structures.

Data availability

The data that support the findings of this study are available within the article and the associated SI.

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Photoswitching molecules functionalized with optical cycling centers provide a novel platform for studying chemical transformations in ultracold molecules:

Supporting Information

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1. DFT BENCHMARKING

Initially, we planned to use Density Functional Theory (DFT) methods, benchmarked previously by some of us using the PBE0 functional with the def2-TZVPPD basis set and

D3 dispersion corrections^{1,2}. However, we soon realized that the types and the order of the excited states produced by the TDDFT calculation did not match EOM-CC values. Table S1 presents the results of a screening of different DFT functionals for *trans*-pAB. The first four excited states are shown, along with their characterized transition orbitals, vertical excitation energies, and oscillator strengths.

All DFT calculations were performed using the *ORCA 6* quantum chemistry package. The RIJCOSX approximation was used, and no random-phase approximation was applied in the TDDFT section of the calculations.³⁻²¹

The only functionals found to produce results in qualitative agreement with EOM-CC are range-separated double-hybrid spin-scaling functionals, namely SOS-wPBEPP86 and SOS-wB88PP86. Unfortunately, these functionals rely on MP2 calculations, which diminishes the appeal of using DFT methods.

TABLE S1. Screening of different DFT functionals. The first four excited states are presented, for each excitation energy and oscillator strengths are reported. State characterization is omitted for non-physical states. All reported DFT calculations use def2-TZVPP basis set. The reference EOM-CC calculation used aug-cc-pVDZ basis set. State energies reported in eV with corresponding oscillator strengths in parentheses.

Method	ES1	ES2	ES3	ES4
PBE0	1.834 (0.0)	1.928 (0.18)	1.933 (0.20)	1.990 (0.00)
	$n \rightarrow \pi^*$	$s \rightarrow p - like$	$s \rightarrow p - like$	$\pi \rightarrow \pi^*$
B3LYP	1.900 (0.0)	1.945 (0.04)	2.049 (0.00)	2.058 (0.19)
	$n \rightarrow \pi^{**}$	$s \rightarrow \pi^{**}$	$\pi \rightarrow \pi^{**}$	$s \rightarrow \pi^*$
TPSS0	1.862 (0.21)	1.866 (0.19)	1.871 (0.00)	1.908 (0.00)
	$s \rightarrow \pi^*$	$s \rightarrow \pi^*$	$n \rightarrow \pi^{**}$	$\pi \rightarrow \pi^{**}$
CAM-B3LYP	1.975 (0.0)	1.980 (0.0)	2.016 (0.19)	2.022 (0.19)
	$n \rightarrow \pi^{**}$	$\pi \rightarrow \pi^*$	$s \rightarrow \pi^*$	$s \rightarrow \pi^*$
wB2PLYP	3.373 (0.0)	2.058 (0.22)	2.079 (0.00)	2.076 (0.23)
		$s \rightarrow \pi^*$	$n \rightarrow \pi^{**}$	$s \rightarrow \pi^*$
wB2GP-PLYP	2.532 (0.0)	2.069 (0.23)	2.090 (0.25)	2.152 (0.0)
		$s \rightarrow \pi^*$	$s \rightarrow \pi^*$	$n \rightarrow \pi^{**}$
wPBEPP86	2.679 (0.01)	2.067 (0.24)	2.090 (0.25)	2.122 (0.0)
		$s \rightarrow \pi^*$	$s \rightarrow \pi^*$	$n \rightarrow \pi^{**}$
DSD-BLYP/2013 D3BJ	4.228 (0.00)	2.310 (0.27)	2.335 (0.28)	2.985 (0.33)
		$s \rightarrow \pi^*$	$s \rightarrow \pi^*$	$s \rightarrow d_{z^2}$
SOS-WPBEPP86	2.059 (0.25)	2.078 (0.26)	2.278 (0.00)	2.278 (0.24)
	$s \rightarrow p$	$s \rightarrow p$	$s \rightarrow d$	$n \rightarrow \pi^{**}$
SOS-wB88PP86	2.051 (0.25)	2.051 (0.25)	2.276 (0.00)	2.257 (0.24)
	$s \rightarrow p$	$s \rightarrow p$	$s \rightarrow d$	$n \rightarrow \pi^{**}$
EOM-EA-CCSD	1.964 (0.26)	1.983 (0.27)	2.271 (0.25)	2.943 (0.00)
	$s \rightarrow p$	$s \rightarrow p$	$s \rightarrow d$	$s \rightarrow d$

TABLE S2. FCF for tpAB A→X fluorescence.

FCF	transition
0.858	A(0) → X(0)
0.037	A(0) → X(1v10)
0.027	A(0) → X(1v2)
0.024	A(0) → X(1v6)
0.013	A(0) → X(1v8)
0.009	A(0) → X(1v17)
0.005	A(0) → X(1v4)
0.004	A(0) → X(1v50)
0.005	A(0) → X(1v29)
0.003	A(0) → X(1v22)
0.001	A(0) → X(1v2,1v10)
0.001	A(0) → X(1v6,1v10)

2. FRANCK-CONDON FACTORS

With potential future applications in mind, we computed Franck-Condon factors (FCFs). FCFs are overlaps between initial and final vibrational states:

$$f_{\nu\mu} = \langle \chi_{\nu}^f | \chi_{\mu}^i \rangle. \quad (1)$$

We computed the FCFs using the vertical gradient (VG) method as implemented in the ezFCF package²². At the optimized EOM-EA-CCSD/cc-pVDZ geometry for the ground state, we calculated the harmonic frequencies and modes for the ground state. At the same geometry with the same method we then calculated the gradient for the excited state. VG approximation finds the equilibrium geometries for the excited state. We use that excited state geometry for the parallel approximation harmonic simulation of the FCFs.

The FCFs for the tpAB molecule are collected in Table S2. Mode 10 (366 cm⁻¹) is a Ca-O stretch. Mode 2 (38 cm⁻¹) is the Ca-O-AB bend in plane. Mode 6 (186 cm⁻¹) is a mixture of a C-N-N-C squeezing and a Ca-O stretching. Mode 8 (266 cm⁻¹) is similar to mode 6.

The FCF for cpAB emission from the ground vibrational state of the A state are collected

in Table S3. Mode 9 (298 cm^{-1}) is in a leading way the Ca-O stretch but it also involves motion in the rest of the molecule. Mode 1 (43 cm^{-1}) is a Ca-O-C bend, but it also involves rotation of the remote phenyl ring. Mode 2 is also a bend of the Ca-O-C part that is coupled to the motion of the reminder of the molecule.

TABLE S3. FCFs for cpAB A→X fluorescence.

FCF	transition
0.806	A(0) → X(0)
0.055	A(0) → X(1v1)
0.047	A(0) → X(1v9)
0.016	A(0) → X(1v2)
0.008	A(0) → X(1v7)
0.006	A(0) → X(1v3)
0.005	A(0) → X(1v16)
0.004	A(0) → X(1v17)
0.004	A(0) → X(1v14)
0.004	A(0) → X(1v50)
0.003	A(0) → X(1v29)
0.003	A(0) → X(1v4)
0.003	A(0) → X(1v1,1v9)
0.002	A(0) → X(1v0)
0.002	A(0) → X(1v5)
0.002	A(0) → X(2v1)
0.002	A(0) → X(1v10)
0.002	A(0) → X(1v13)
0.002	A(0) → X(1v15)
0.002	A(0) → X(1v30)
0.001	A(0) → X(1v1,1v2)
0.001	A(0) → X(2v9)
0.001	A(0) → X(1v23)
0.001	A(0) → X(1v54)

3. RELEVANT CARTESIAN GEOMETRIES

Optimized geometries of the studied molecules.

25

tpAB, X, EOM-EA-CCSD/cc-pVDZ, Nuclear Repulsion Energy = 1011.18396213 Ha

C	5.3832949554	1.1268023932	-0.0000000000
C	3.9857848754	1.0242652883	-0.0000000000
C	6.1864366870	-0.0311896649	0.0000000000
C	5.5825967915	-1.2986615016	0.0000000000
C	4.1810701040	-1.4061755307	0.0000000000
C	3.3823631861	-0.2507216815	-0.0000000000
N	1.9614847270	-0.4835236846	-0.0000000000
N	1.2812134824	0.5744215944	-0.0000000000
C	-0.1339985068	0.3649235430	-0.0000000000
C	-0.9257923961	1.5257693382	-0.0000000000
C	-2.3247269471	1.4417831343	0.0000000001
C	-2.9688065782	0.1818510535	0.0000000000
C	-2.1571876382	-0.9857954463	-0.0000000000
C	-0.7640421169	-0.8992048201	-0.0000000001
H	5.8537616426	2.1167460216	-0.0000000000
H	3.3494475397	1.9129885234	-0.0000000001
H	7.2785746364	0.0584934720	0.0000000000
H	6.2000128737	-2.2038310242	0.0000000001
H	3.6827083791	-2.3812968442	0.0000000001
H	-0.4209780821	2.4983115557	0.0000000000
H	-2.9389457145	2.3492456808	0.0000000001
H	-2.6524563713	-1.9638216298	-0.0000000000
H	-0.1447973927	-1.8007567674	-0.0000000001
O	-4.3059650637	0.0857744134	0.0000000000
Ca	-6.4134084937	-0.0683092669	0.0000000000

25

cpAB, X, EOM-EA-CCSD/cc-pVDZ, Nuclear Repulsion Energy = 1070.68731908 Ha

C	2.6781911187	-1.7756773868	-1.2763959690
C	2.4057235373	-0.4046638393	-1.1512733827
C	3.4588997986	-2.4380817126	-0.3118390466
C	3.9917334619	-1.7144238678	0.7690647817
C	3.7479526134	-0.3358675487	0.8827525478
C	2.9263566315	0.3099010754	-0.0563771273
N	2.7996008146	1.7528834600	0.0526783944
N	1.6825562332	2.3225413788	0.0523575229
C	0.4341513897	1.5835562463	0.0752758955
C	-0.5897558499	2.0732921462	-0.7541272382
C	-1.8560458532	1.4742368630	-0.7567668371
C	-2.1528722867	0.4053131171	0.1236385311
C	-1.1297503516	-0.0370198315	0.9989495106
C	0.1475839200	0.5360767829	0.9720632202

H	2.2747285899	-2.3305092641	-2.1309847067
H	1.7914396841	0.1112218491	-1.8961246432
H	3.6619771828	-3.5101034326	-0.4104190551
H	4.6149450286	-2.2194968328	1.5156033542
H	4.1824488983	0.2511047765	1.6992698212
H	-0.3735716924	2.9261719430	-1.4075532441
H	-2.6441103785	1.8434881736	-1.4229081613
H	-1.3553981905	-0.8449428646	1.7044090349
H	0.9173910708	0.1730687125	1.6600598445
O	-3.3697643668	-0.1613755506	0.1412332454
Ca	-5.2816560827	-1.0567832255	0.1711274484

26

trans-bpAB, X, EOM-SF-CCSD/cc-pVDZ, Nuclear Repulsion Energy = 1294.26301641 Ha

N	-0.3420305297	-0.5282212074	0.0000000000
N	0.3420892032	0.5284770910	0.0000000000
C	-1.7570868236	-0.3055700695	0.0000000000
C	1.7570905269	0.3057352686	0.0000000000
C	-2.3765288730	0.9629748805	0.0000000000
C	-2.5590997234	-1.4590706309	-0.0000000000
C	2.3764213087	-0.9628732575	0.0000000000
C	2.5592092426	1.4591698524	-0.0000000000
C	-3.7702655116	1.0620727324	0.0000000000
C	-3.9582052229	-1.3631196093	-0.0000000000
C	3.7701319876	-1.0620990062	0.0000000000
C	3.9582914276	1.3630962797	-0.0000000000
C	-4.5865776836	-0.0982770135	-0.0000000000
C	4.5866055545	0.0981844819	-0.0000000000
H	-1.7496016471	1.8590216858	0.0000000000
H	-2.0624483455	-2.4356512007	-0.0000000000
H	1.7494092693	-1.8588648518	0.0000000000
H	2.0626421764	2.4357961439	-0.0000000000
H	-4.2568698354	2.0442001609	0.0000000000
H	-4.5803368187	-2.2649536161	-0.0000000000
H	4.2566585798	-2.0442633513	0.0000000000
H	4.5805116926	2.2648670630	-0.0000000000
O	-5.9517762260	0.0107822454	-0.0000000000
Ca	-8.1286608483	0.1772514427	0.0000000000
O	5.9516859442	-0.0109945681	-0.0000000000
Ca	8.1287411755	-0.1776709460	-0.0000000000

26

cis-bpAB, X, EOM-SF-CCSD/cc-pVDZ, Nuclear Repulsion Energy = 1382.87508439 Ha

Ca	5.3866142952	0.1436922329	2.8385157117
O	4.0227292881	0.0781350219	1.1396407606
C	3.1740867799	0.0490540576	0.0631975122
C	3.3104847626	-0.9343595776	-0.9426039650
H	4.1142648631	-1.6740139194	-0.8555623751
C	2.4529428524	-0.9431659667	-2.0521036765

H	2.5826471999	-1.6811202467	-2.8518819539
C	1.4026255211	-0.0157359562	-2.1524339573
C	1.2689787786	0.9801548663	-1.1662841441
H	0.4793434901	1.7336324845	-1.2512979194
C	2.1486929605	1.0139586367	-0.0765745203
H	2.0505161817	1.7940138967	0.6868457780
N	0.6261485492	-0.0390497739	-3.3787156263
N	-0.6261485492	0.0390497739	-3.3787156263
C	-1.4026255211	0.0157359562	-2.1524339573
C	-2.4529428524	0.9431659667	-2.0521036765
H	-2.5826471999	1.6811202467	-2.8518819539
C	-3.3104847626	0.9343595776	-0.9426039650
H	-4.1142648631	1.6740139194	-0.8555623751
C	-1.2689787786	-0.9801548663	-1.1662841441
H	-0.4793434901	-1.7336324845	-1.2512979194
C	-2.1486929605	-1.0139586367	-0.0765745203
H	-2.0505161817	-1.7940138967	0.6868457780
C	-3.1740867799	-0.0490540576	0.0631975122
O	-4.0227292881	-0.0781350219	1.1396407606
Ca	-5.3866142952	-0.1436922329	2.8385157117

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