

Photochemistry

Efficient Sensitized $Z \rightarrow E$ Photoisomerization of an Iridium(III)-Azobenzene Complex over a Wide Concentration RangeJavier Moreno,^[a, b] Lutz Grubert,^[a] Jutta Schwarz,^[a] David Bléger,^[a] and Stefan Hecht*^[a]

Abstract: To improve the sensitized $Z \rightarrow E$ photoisomerization of azobenzenes, and circumvent the threshold concentration necessary for the bimolecular photoinduced electron transfer reaction to generate the rapidly isomerizing Z -azobenzene radical anion, an Ir^{III} complex with a covalently teth-

ered azobenzene fragment was synthesized. Selective irradiation of the ¹MLCT band of the Ir^{III} complex induced an efficiently sensitized photoswitching of the dyad over a wide concentration range and even at high dilution.

Introduction

Imparting photoresponsive properties to materials has been a topic of much research in the last decade. Optical modulation of properties and functions enables the design of smart chemical systems that can be externally controlled with high spatial and temporal resolution.^[1] As photochromism research has matured,^[2] an increasing number of photoswitches was prepared, and strategies for their direct or indirect operation have been developed,^[3] thereby enabling their application in the materials^[4] and life^[5] sciences.

In the family of the established azobenzene (AB) photoswitches,^[6] which upon UV-light irradiation undergo an $E \rightarrow Z$ isomerization of the N=N double bond, such important recent developments include that the photoisomerization could be induced by visible light,^[7] and upon direct 2-photon^[8] or indirect 2-photon NIR^[9] excitation. Simultaneously a new orthogonal possibility emerged by the direct use of electrons as an alternative to photons for triggering the reversible isomerization process. For example successful electrochemical switching of diarylethenes was demonstrated in the past.^[10] In the case of AB photoswitches, Laviron and Mugnier already in 1978 showed that in aprotic solvents the Z -isomer could be reduced

to the radical anion, which rapidly isomerized to the E -isomer.^[11] These observations implied that catalytic amounts of electrons suffice to trigger quantitative $Z \rightarrow E$ conversion, which was recently proven by us and shown to be a general feature of AB photoswitches.^[12] Furthermore, controlling the electrochemical switching process by coupling it to an indirect source of electrons, for example, a photosensitizer, enabled the control of the electrocatalytic $Z \rightarrow E$ isomerization with light. However, the efficiency of the system was found to be dependent on the concentration of the photosensitizer due to the intermolecular nature of the electron transfer process, requiring a threshold amount of the photosensitizer (10 mol% corresponding to 10^{-4} M) to exert the maximum electrocatalytic effect.^[12]

In our initial work, we have utilized iridium(III)tris(2-phenylpyridine) complexes as photosensitizers due to their advantageous photophysical properties originating from their triplet manifold^[13] in combination with their redox levels matching the AB reduction potential.^[14] In order to further enhance the efficiency of our photoswitchable system we sought to covalently tether the Ir-based photosensitizer to the AB photochromic unit. Although several coordination compounds derived from AB scaffolds are known,^[15] only few exploit the sensitizing properties of the transition-metal complex to mediate or promote the photoisomerization of the photoswitch.^[16]

Here, we report the synthesis and characterization of an Ir^{III} complex bearing a thermally stable acetylacetonato-AB ligand and capable of undergoing an efficient photosensitized $Z \rightarrow E$ isomerization over a wide concentration range and even concentrations below 10^{-5} M.

Results and Discussion

Synthesis

For the design of our target compound, it is important to utilize *ortho*-fluorinated ABs, since their $E \rightarrow Z$ photoisomerization can be triggered with visible light ($\lambda > 500$ nm),^[3b, 7e, i] thereby

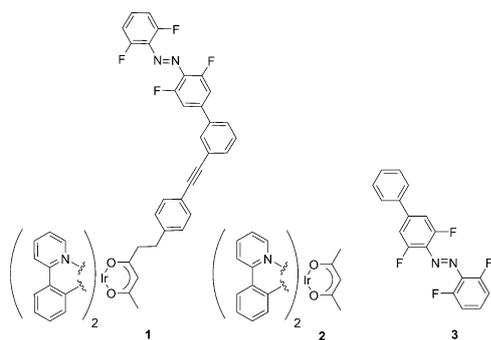
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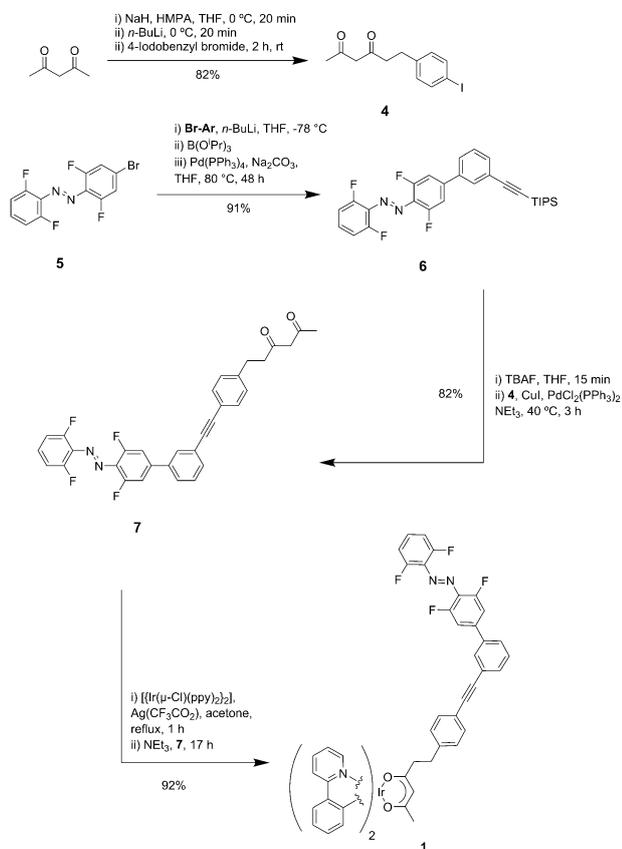
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enabling selective excitation in the presence of the Ir^{III} complex that sensitizes the reverse process. More importantly, the exceptionally long thermal half-life^[3b,7e,i] facilitates the study of *Z*→*E* sensitized isomerization. To maintain their properties, the two components have to be linked in a covalent fashion, which precludes their electronic and steric interaction, and hence a cross-conjugated *meta*-phenylene unit was introduced. The resulting target construct **1** as well as the individual components **2** and **3**, serving as reference compounds, are depicted in Scheme 1.

The synthesis of **1** was accomplished following a modular approach (Scheme 2). Regioselective nucleophilic addition of acetylacetone to 4-iodobenzyl bromide was achieved by the



Scheme 1. Ir(ppy)₂acac-AB complex **1** and reference compounds **2** and **3**.



Scheme 2. Synthesis of Ir(ppy)₂acac-AB complex **1**.

stepwise formation of the disodiumenolate of acetylacetone (acac) with NaH in THF at 0 °C assisted by hexamethylphosphoramide (HMPA), which promotes the subsequent fast metal exchange with *n*BuLi at the 1-position. Reaction with 4-iodobenzyl bromide provided the ligand fragment **4** in a good yield of 82%. Synthesis of the AB-containing coupling partner **6** in a high yield of 91% was accomplished by Suzuki cross-coupling of 4-bromo-2,2',6,6'-tetrafluoroazobenzene **5**^[8] to the boronic ester of the *meta*-phenylene ethynylene triisopropylsilyl-protected linker, prepared through a lithiation/borylation sequence. Protodesilylation of **6** with tetra-*n*-butylammonium fluoride followed by Sonogashira coupling of the obtained AB-containing alkyne with acac-derived building block **4** afforded the desired ligand **7** in a good yield of 82%.

To increase the reactivity of the Ir^{III} center towards ligand **7**, the commercial dimeric species of {Ir(μ -Cl)(ppy)₂}₂ was refluxed with Ag(CF₃CO₂) for 17 h to yield a monomeric Ir^{III} complex with labile trifluoroacetato ligands. After removal of the precipitated AgCl, ligand **7** and triethylamine were added, and it was stirred for 17 h at room temperature before TLC analysis indicated quantitative complex formation. After work-up and purification, involving initial column chromatography on Al₂O₃, separation of minor Ir^{III} impurities by gel permeation chromatography (GPC) and final column chromatography on Al₂O₃ followed by additional recrystallization from petroleum ether, yielded the target compound **1** in an excellent yield of 92%.

UV/Vis spectroscopy

The UV/Vis absorption spectra of complex **1**, in both the *E*- as well as *Z*-configuration, resemble the spectral signatures of both individual components as seen by comparison with the sum spectra of reference compounds **2** and **3** (Figure 1, Figure S12 in the Supporting Information). The long wavelength absorption maxima at 456 nm (*E*-1) and 406 nm (*Z*-1) are assigned to the characteristic *n*→ π^* band of the *ortho*-fluorinated azobenzene, combined with MLCT bands arising from the Ir^{III} fragment. The MLCT absorption bands at 407 nm and 440 nm are associated with the complex and exhibit no spectral change upon photoisomerization, further illustrating decoupling of the two chromophore subunits in the ground state of both isomers. Compound **1** displayed reversible photochromism and exhibited very high *Z*-isomer content in the photostationary state (PSS) obtained upon vis-light irradiation (Figure 1, Figure S17 in the Supporting Information). The absorptivities and composition at the PSS of compound **1** in acetonitrile are depicted in Table 1. Upon irradiation with green light ($\lambda > 500$ nm) the *n*→ π^* band of the *E*-form is selectively addressed enabling to achieve a very high PSS in compound **1**, with similar values to those for the previously reported *ortho*-fluorinated ABs.^[7e,i,8,9] It can be thus assumed, that the Ir^{III}-antenna has negligible electronic influence on the *n*→ π^* band of the AB, ensuring the possibility to selectively address with light the individual components of compound **1**. Since the overlap of the absorption spectra between the AB and the Ir^{III} complex is severe in the UV region, it is difficult to assign the proper transitions of **1**. However, because the coupling did not

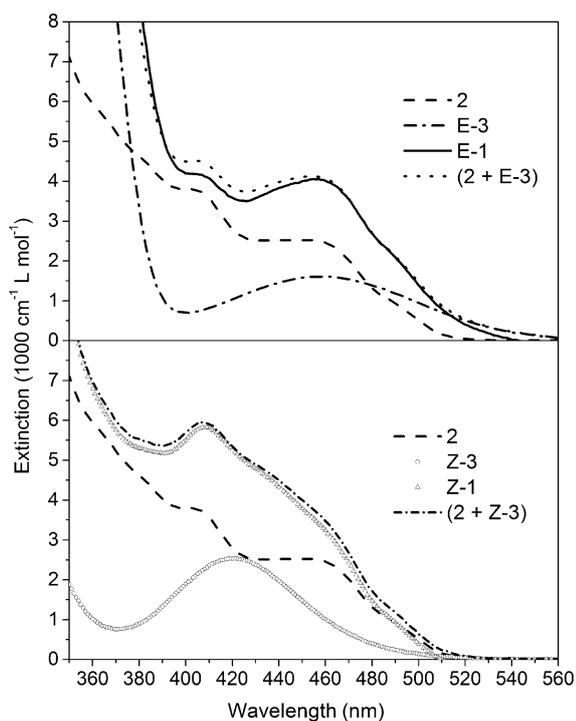


Figure 1. UV/Vis spectra in acetonitrile of *E*-1 (black line), calculated *Z*-1 (empty triangles), **2** (dashed line), *E*-3 (dash dotted line), and calculated *Z*-3 (empty circles) (10^{-5} M, 25 °C). Direct sum of spectra (**2** + *E*-3, dotted black line) or (**2** + *Z*-3, short dash dotted line) agree with the spectra of the complex **1**, suggesting a weak coupling of the Ir^{III} fragment and the azobenzene in the ground state.

	λ_{\max} [nm] (ϵ [10^3 L mol ⁻¹ cm ⁻¹])		PSS _{vis} [Z:E]	PSS _{380 nm} [Z:E]	PSS _{365 nm} [Z:E]
	<i>E</i>	<i>Z</i>			
1	456 (4.05)	407 (5.82)	89:11	24:76	47:53
3	457 (1.60)	421 (2.54)	95:5	77:23	90:10

influence the electronic properties of the AB moiety, we can assume that the assigned transitions of **2** will be in the same spectral region for **1** (Figure S13 in the Supporting Information). The transitions were assigned in accordance with the literature^[16] and in analogy to [Ir(ppy)₃].^[13a] Strong bands in the region below 310 nm are thus attributed to allowed $\pi \rightarrow \pi^*$ transitions of the ligands and correspond to singlet ligand-centered (¹LC) states. On the other hand, absorption bands occurring above 320 nm arise mainly from Ir5d-(ppy) π^* transitions corresponding to singlet metal–ligand charge transfer (¹MLCT) states. The weak shoulder in the range of 440–480 nm is attributed to the corresponding ³MLCT states. The fact that the absorption into the lowest triplet state *T*₁ is observed is remarkable and is indicative of a strong mixing of MLCT states, typical for [Ir(ppy)_{*n*}] complexes.^[13a]

Fluorescence spectroscopy

In analogy to similar compounds, the emissive state starting at 480 nm and reaching emission maximum at 526 nm is assigned to be predominantly of ³LC character with little ¹MLCT partitioning. However, in strong contrast to the behavior in the ground state, efficient communication between the Ir^{III} center and the AB moiety in the complex was observed, since the emission intensity was completely suppressed by 96% in compound **1** (Figure S13 in the Supporting Information). This observation was further manifested by the much lower fluorescence quantum yield measured for **1** in acetonitrile ($\Phi = 0.01$) as compared to complex **2** ($\Phi = 0.34$).^[17] The negligible fluorescence emission of the Ir^{III} unit in **1** (at low concentrations) is clear evidence for an efficient (intramolecular) quenching process. Upon photoisomerization, the shape of the emission band of the *E*-1 and *Z*-1 isomers remains unaffected (Figure S14 in the Supporting Information).

(Spectro)electrochemistry

To evaluate the thermodynamic feasibility of a photoinduced electron transfer (PET) process the redox potentials of compounds **1–3** were measured using cyclic voltammetry (CV). The obtained cyclic voltammograms show that compounds **1** and **2** undergo fully reversible one-electron oxidation and reduction, whereas compound **3** undergoes fully reversible reduction (Figure S18, Table S2 in the Supporting Information). The reduction potential of the parent (ppy)₂Ir(acac) complex **2** is considerably higher than that of the parent AB **3**, suggesting PET from the sensitizing complex to the AB ligand as the origin of fluorescence quenching in **1** upon ¹MLCT excitation. However, the obtained reduction potential from CV that is somewhat reminiscent of the LUMO level only serves as an approximation since PET most likely proceeds from the first excited triplet state *T*₁ due to its much longer lifetime as compared to the first excited singlet state *S*₁ because of efficient intersystem crossing (ISC). Assuming that PET would proceed from the *T*₁ state, the Ir^{III} moiety would act as the electron donor, and the *Z* AB unit would serve as the acceptor.

When the CV of compound *Z*-1 was measured, only the cathodic peak assigned to the pure *E*-isomer was detected.^[12] Following Hapiot's methodology,^[18] very fast scan rates were employed and combined with spectroelectrochemistry, to record the spectral evolution upon increasing applied negative potential for *Z*-1 (Figure 2).

As implied from the top inset of Figure 2, at lower negative potentials a small reduction process occurs (top inset, Figure 2), which, once initiated at very low current values, converts the *Z*-1 solution quantitatively to *E*-1.^[12,19] Subsequent increase of the applied negative potential promotes the reduction of the electrochemically generated *E*-1 to the radical anion (bottom inset, Figure 2) with the corresponding spectral signature appearing at 448 nm and 575 nm. The same behavior was observed for the reference compound *Z*-3 (Figure S19 in the Supporting Information), suggesting that the electrochemical reduction of the *Z*-AB moiety in **1** is indeed a catalytic

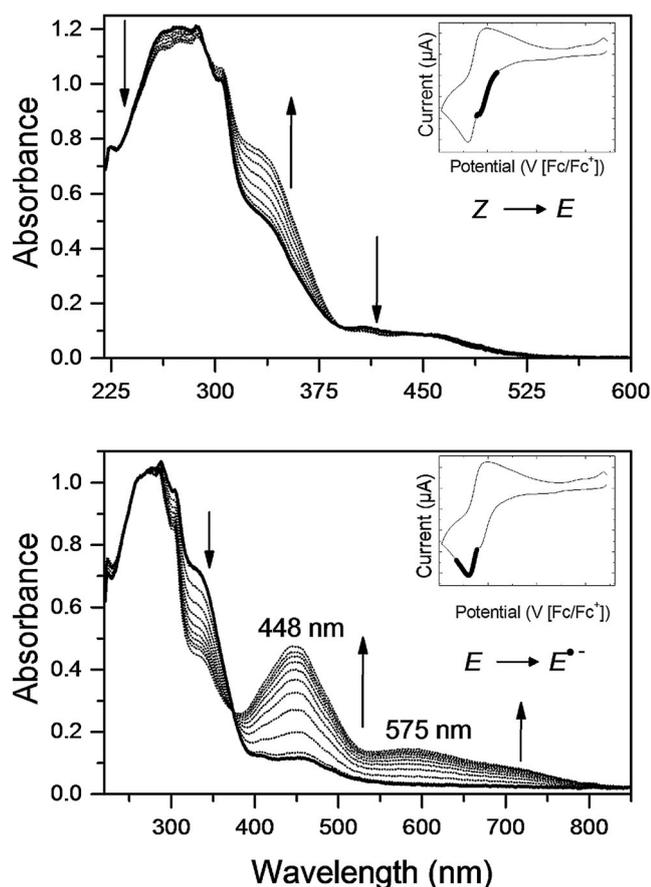


Figure 2. Spectral evolution starting from a Z-1 enriched solution (black line, top) in acetonitrile 0.1 M Bu₄NPF₆ upon increasing applied negative potential corresponding to inset black line (top). Continued spectral evolution after electrochemical isomerization of Z-1 → E-1 (black line, bottom) upon increasing applied negative potential corresponding to inset black line (bottom).

process, as shown by us recently.^[12] This process can be promoted under an applied negative potential at the conditions employed in the SEC and CV measurements. Since the HOMO and LUMO levels enable a PET from the excited sensitizer to the ground state of the Z-AB moiety, this mechanism could explain the observed photophysical properties of compound 1 upon ¹MLCT (380 nm) excitation.

Photoinduced isomerization

Driven by our spectroscopy and (spectro)electrochemistry investigations of 1, and in conjunction with our previous findings associated to the indirect photoinduced Z → E isomerization of ABs,^[9,12] we wanted to evaluate the advantage of rendering the photoinitiation step (PET) intramolecular, and hence concentration-independent.

Assuming a PET from the excited Ir^{III} fragment to the AB moiety to be the origin of the observed fluorescence quenching, Z → E photoisomerization experiments were conducted with compound 1 and reference 3 using 380 nm UV-light irradiation (Figure S16 in the Supporting Information). When the highly Z-enriched PSS mixtures were subjected to identical irradiation conditions and quantified by ultra performance liquid

chromatography (UPLC), Z → E isomerization in 1 was much faster and more efficient ($\Phi_{ZE}(1) = 0.28$) as compared to the reference AB 3 ($\Phi_{ZE}(3) = 0.18$) and a higher E-isomer content in the PSS was achieved (for example 53% E-1 vs. 23% E-3 in Figure S16 of the Supporting Information). Furthermore, differential spectra were calculated for 1 and 3 and show an analogous spectral-shape evolution for both compounds (middle, Figure S16 in the Supporting Information), thereby corroborating the ground-state decoupling between the Ir^{III} center and the AB ligand, and promoting the efficient PET between the two in complex 1.

Upon 365 nm irradiation the parent AB 3 could be isomerized to a remarkably low E-isomer content of only 10%, independent of the initial Z-form content (Figure 3, bottom). How-

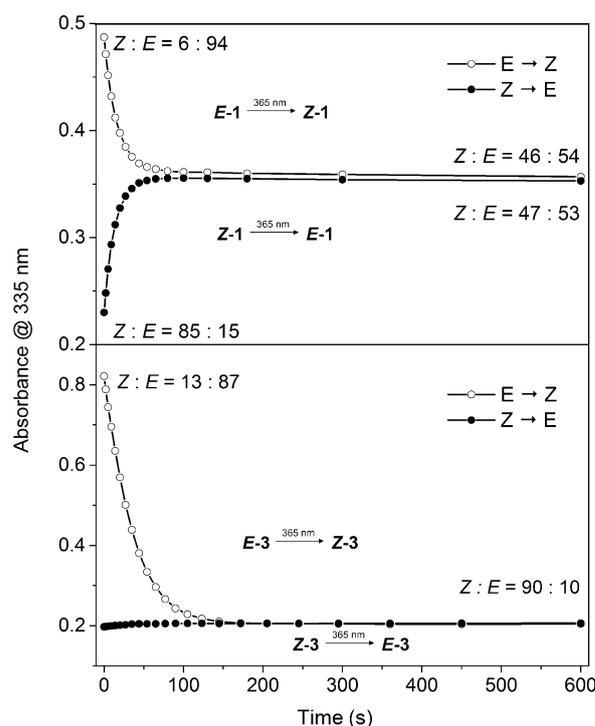


Figure 3. E- (empty circles) and Z- (full circles) isomer evolution induced by irradiation with 365 nm versus irradiation time in seconds for 1 (top) and 3 (bottom) in acetonitrile.

ever, identical irradiation conditions in the case of complex 1 gave rise to a much higher E-isomer content of 54% (Figure 3, top), demonstrating the mechanistically different isomerization pathway operating and dominating in the sensitizer AB dyad.

In order to evaluate the concentration dependence of the photosensitized Z → E isomerization in the case of our covalent Ir^{III}-AB construct, degassed acetonitrile solutions of decreasing concentration of 1 were prepared. Irradiation at 500 nm was used to prepare Z-enriched solutions (black squares, Figure 4), and their subsequent irradiation at 380 nm allowed us to determine the E-isomer content (empty circles, Figure 4).

As expected and as evident from Figure 4 the intramolecular PET process exhibits rather little concentration dependence and, most importantly, it remains efficient even in highly dilute

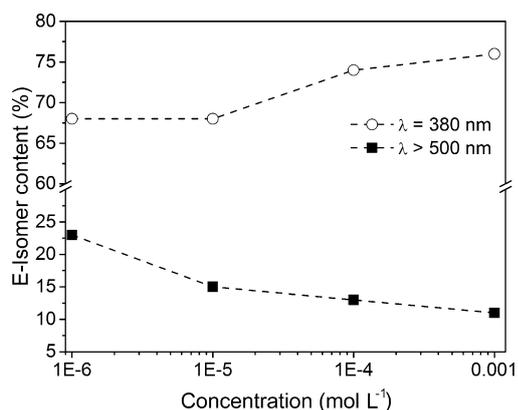


Figure 4. Concentration dependence of photosensitized $Z \rightarrow E$ isomerization: Initial $E-1$ content in the PSS of a degassed Z -enriched mixture in acetonitrile obtained after 500 nm irradiation (black squares) and final $E-1$ content in the PSS after irradiation with 380 nm (empty circles) as monitored by UPLC.

solutions, in which intermolecular PET becomes inefficient.^[12] Furthermore, exhaustive degassing of the sample led to higher E -isomer content after 380 nm irradiation ($\approx 70\%$ $E-1$ vs. 53% $E-1$ without degassing), indicating that O_2 acts as a competing quencher of the triplet excited Ir^{III} complex.

Conclusion

A novel Ir^{III} complex containing a photochromic AB ligand was designed and synthesized. Photoswitching of the AB moiety was retained and could be induced by direct excitation of its well-separated $n \rightarrow \pi^*$ bands. Comparison of the spectroscopic and electrochemical features of the complex with the known $Ir(ppy)_3$ showed that there is no electronic communication between the metal center and the AB unit in the ground state. Spectroelectrochemistry verified reductively induced (catalytic) $Z \rightarrow E$ isomerization and irradiation of the 1MLCT band at 380 nm also induced $Z \rightarrow E$ isomerization. All relevant photo- and electrochemical processes are summarized in Figure 5. From the estimated energy levels of the components, the PET process, which leads to emission quenching and subsequent $Z \rightarrow E$ isomerization appears to be the most likely mechanism. The alternative scenario, involving PET from the excited AB to the Ir^{III} center followed by formation and isomerization of the AB radical anion, can be ruled out due to the negligible extinction coefficient of the AB at 380 nm when compared to the $Ir(ppy)_2$ unit.

By establishing a thermodynamically favorable sensitization pathway through an indirect PET mechanism and by covalently linking the PET sensitizing Ir^{III} complex to the AB, we have created a system that can isomerize very efficiently even at concentrations below 10^{-5} M. Of course, the covalent construct is only able to promote the initial intramolecular PET step. Subsequent propagation of the catalytic chain does not take place (at least to a large extent), since it would involve intermolecular electron transfer steps and hence requires a threshold concentration while competing with the efficient intramolecular back electron transfer step. Current and future work is focused

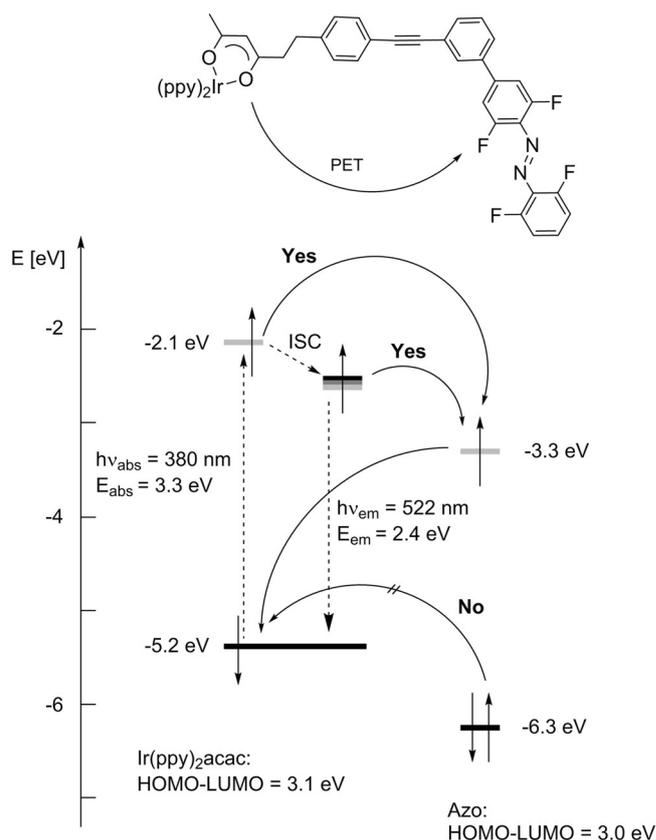


Figure 5. Energy levels of the individual dyad components in acetonitrile: Solid lines represent electron transfer steps. HOMO (black) and LUMO (grey) levels originate from experimental CV data, triplet (shadowed black) energy level of the dyad has been extrapolated from emission data.

on the elucidation of the switching mechanism by characterizing the involved intermediates by transient absorption spectroscopy, and by identifying other more redshifted, ideally purely organic, photosensitizing units.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: azobenzene • iridium complexes • photochromism • photoinduced electron transfer • spectroelectrochemistry

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