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Mesityl or Imide Acridinium PhotoCatalysts: Accessible versus not Accessible Charge-Transfer State in Photoredox Catalysis

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Abstract: A study on the C9-imide acridinium photocatalysts with enhanced photoredox catalytic activity with respect to the well-established C9-mesityl acridinium salt is presented. The differences observed rely on the diverse accessibility of singlet charge-transfer excited states, which have been proved by CASPT2/CASSCF calculations, fluorescence and quenching studies.

In recent years, visible-light organo-photoredox catalysis^[1] has arisen as a valid and potent alternative for the commonly used photoredox catalysts based on ruthenium and iridium polypyridyl complexes.^[2] Indeed, these organo-catalysts have opened new paths in visible light-induced photoredox processes, due to their versatility, the wide range of reductive and oxidative potentials and their reasonable prices.^[3] In this regard, the acridinium-based photoredox catalysts **1**¹ (Figure 1, left) have

attracted a vast interest, especially in the form of the corresponding 9-mesityl derivatives. Indeed, from the pioneering work of Fukuzumi and co-workers,^[4] the 9-mesityl *N*-methyl acridinium salt (**1b**) was found to be one of the most powerful photoredox catalysts.^[5] In the last decade, **1b** became the most widely used acridinium-based photoredox catalyst due to its stability and its high oxidative potential (~2.2 V vs. SCE). However, it still presents substantial reactivity and stability limitations.^[1,4,5] Aiming at overcoming some of these restraints, we recently developed a new class of C9-imide acridinium-based photoredox catalysts (**2**, Figure 1, top).^[6] In this manner, a vast library of imide-acridinium derivatives with comparable or even improved properties than **1b** was achieved. The *N*-methyl and *N*-phenyl cyclohexyl derivatives (**2a** and **2b**) showed the highest efficiency as photoredox catalysts in all the reactions we tested, showing in all the cases better results than employing **1b** (Figure 1, bottom). The mesityl group of **1b** is responsible of the low susceptibility to nucleophilic and radical addition on the acridinium core of **1b**, increasing its chemical stability. However, this orthogonal electron-rich aromatic ring in the C9-position opens the access to inactive charge transfer species (CT).^[4,7-10] The role of these charge-transfer states has been a matter of debates,^[7] but at the moment it is accepted that the singlet charge transfer (CT^s) state is irrelevant in electron-transfer processes and it is an unproductive photoredox pathway.^[1,8] Therefore, its tendency is to decay via non-radiative pathways or to perform the intersystem-crossing.

In this work, in order to get some insight on the better performance of the novel class of acridinium salt catalysts **2** respect to the classical mesityl derivatives **1**, we have investigated the photophysics of both the Fukuzumi's catalyst **1b** and the acridinium salts **2** with the help of steady state spectroscopy and excited state ab initio simulations.

We started measuring and comparing the properties connected to long life and active singlet excited species of **1** and **2** (Table 1). In principle, both triplet-states, the charge transfer triplet state (CT^T) and the locally excited triplet (LE^T) could take part on electron transfer (ET) processes.^[4,10] However, under the standard concentrated conditions the quenching of the triplet state by the reactants was not observed, even when the CT^T state of C9-mesityl acridinium photocatalyst was recently reported to be active in particular cases, exhibiting both oxidizing and

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reducing abilities.^[11] Therefore, the triplet contribution is almost negligible.^[8a] As a result, it is evident that the insertion of a mesityl group in the 9-position on an acridinium scaffold is at the same time an advantage and a drawback: on one hand it enhances the stability of the acridinium core; on the other hand it decreases the fluorescence quantum yield and life time of excited species due to the access to unproductive CT states (Table 1). As a matter of fact, we wondered about the effect of introducing the bulky C9-imide group of **2a-b** in the population of CT states. Therefore, additional experimental and theoretical evidences were needed in order to clarify this issue.

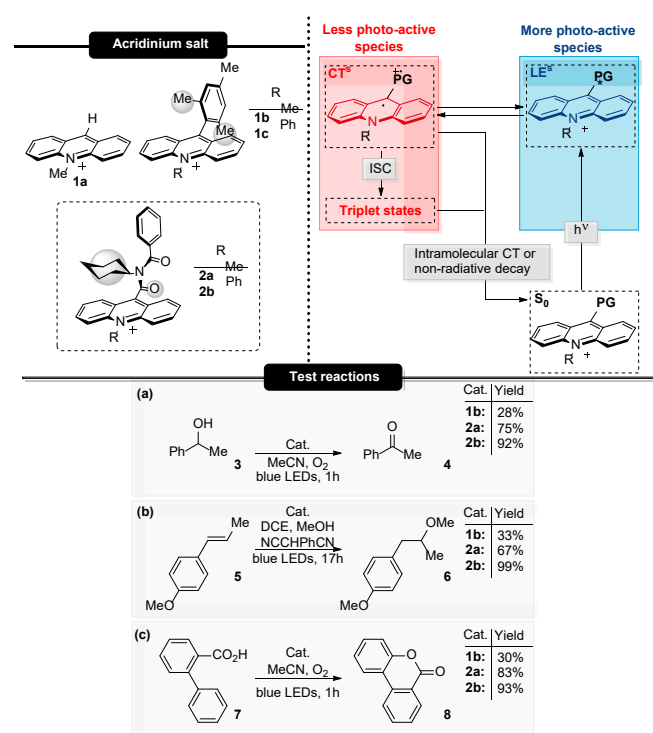


Figure 1. Acridinium salt catalysts and their theoretical photo-excited species (PG= Protecting Group) (top). Test reactions (bottom).

The absorption spectra were first recorded for all the acridinium salts (Figure 2, left). The maximum absorbance in the visible light region for all the catalysts is in the range of 420–450 nm. Moreover, since **1a** is known to have an extremely high fluorescence quantum yield ($\Phi_F \sim 1$),^[12] the four catalysts were compared based on this information. When the catalysts **2a** and **2b** were separately excited with monochromatic light at 430 nm, a significant emission band centred at 500 and 530 nm was observed, respectively (Figure 2, right). The large bathochromic shift of **2b** could be related to the partial planarization of the *N*-Ph caused by the hindrance of the rotation of the bulky imide protecting group.^[13]

The fluorescence quantum yield (Φ_F) of **2a** and **2b** resulted consistently higher ($\Phi_F = 0.10$ and 0.25 , respectively) compared to the Fukuzumi acridinium salt **1b** ($\Phi_F = 0.02$) (Table 1). Such

characteristics, as the fluorescence lifetime and quantum yield, were substantially lower for **1b** than for **1a**. This is ascribed to the impossibility of **1a** to form CTs species due to the absence of substituents at the C9 position ($R = H$) (Table 1 and see computational studies below).^[1,4,7] Interestingly, the fluorescence lifetime (τ_F) for **2b** was 12.4 ns, which is notably longer than the τ_F for **1b** (5.1 ns) but still lower than the extremely long lifetime of

Table 1. Photophysical and photoredox data of **1a-b** and **2a-b** photocatalysts considered in this work, and **1c** for comparison reasons.

Cat.	$E^{1/2}_{red}[a]$ (V vs SCE)	$E^{S_{red}}[b]$ (V vs SCE)	$\lambda_{em\ max}$ (nm)	$\Phi_F[c]$	$\tau_F[d]$ (ns)
1a	-0.46	+2.32	490	~ 1	34.7
1b	-0.49	+2.18	507	0.02	5.1
1c ^[14]	-0.55	+2.00	509 ^[e]	n.a.	0.49/5.5 ^[f]
2a	-0.33	+2.36	500	0.10	2.1 ^[g]
2b	-0.28	+2.40	525	0.25	12.4

[a] Ground state reduction potential. [b] Singlet excited state reduction potential. [c] Calculated comparing the fluorescence intensity of **1a**.^[15] [d] Fluorescence half-life time in the presence of air in MeCN. [e] Reported in DCE. [f] Reported in MeOH. [g] Fitting component: 2.1 ns (>99%), 21.8 ns (<1%).

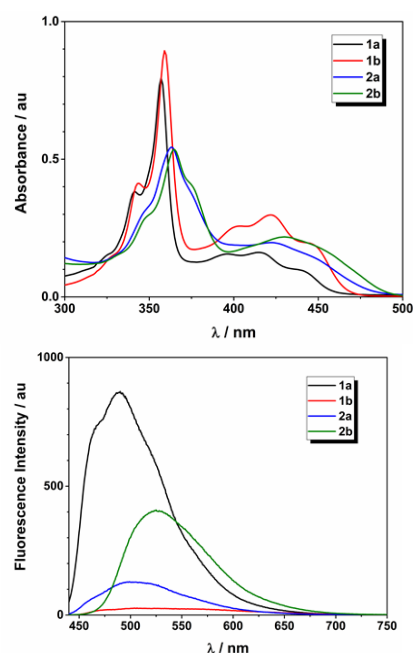


Figure 2. Absorption and emission spectra. [a] Absorption spectra of the corresponding acridinium salt derivatives in acetonitrile under air (left). All concentrations were fixed at 50 μ M; [b] Steady-state emission spectra ($\lambda_{exc} = 430$ nm) of the corresponding acridinium salt derivatives in acetonitrile under air (right). All concentrations were fixed at 50 μ M.

1a excited species (34.7 ns) (Table 1). However, the *N*-Me analogue **2a** presents a lower fluorescence lifetime than the other considered catalysts. Nonetheless, the less rigid 9-imide-based protecting group of the acridinium scaffold has various vibrational and rotational paths that may dissipate the excited state in a non-

radiative manner. In this perspective, taking into account that the excited 9-substituted acridinium scaffold performs a forced bending of the protecting groups in both the 9-position and in the nitrogen,^[16] excited **2a**^{*} could have a higher rotation-freedom than the excited *N*-Ph derivative **2b**^{*}, in which the phenyl group could prevent and block the free rotation of the imide group. This opens more non-radiative decay pathways and, therefore, leads to a lower fluorescence lifetime for the *N*-Me derivative.

Then, the fluorescence of the catalysts **1a-b** and **2a-b** was studied in the presence of a 0.2 M solution of an appropriate quencher such as 1-phenylethanol (**3**, $\sim +2.11$ V vs. SCE)^[17] (Figure 3). The normalized time-resolved emission spectra showed a correlation between the quenching intensity and the light-induced oxidation reaction results when employing different photocatalysts. Indeed, alcohol **3** quenches the excited state of catalyst **2b** (τ_F (**3**) 3.3 ns vs. τ_F 12.4 ns) and slightly that of **1a** and **2a** (Figure 3). This significant dynamic quenching of the singlet excited state for **2b** may rely on its high quantum yield and the initial hypothesis of non-accessible CT and triplet states for this catalyst. Moreover, the emission temporal profile of **1b** retained its characteristic shape under the presence of **3**. This behaviour could be due to the low concentration of singlet excited state of **1b**, which is related to its low fluorescence quantum yield. It is worth to mention that further emission studies under argon showed that **1b** was affected by the presence of air (see S.I.). Therefore, the active excited state from **1b** is less stable under the aerobic reaction conditions, which could contribute to its poor catalytic performance in some systems. Nevertheless, under identical conditions the product **4** is still formed in the presence of **1b** (Figure 1(a), 28%), for which the thermodynamic driving force for an electron transfer process became important.

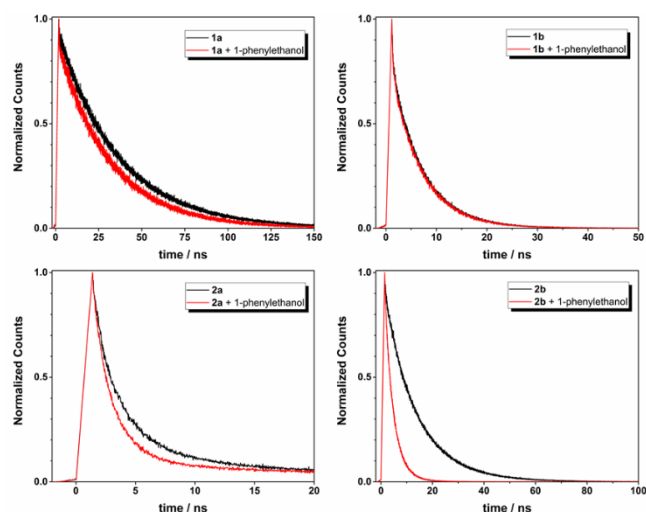


Figure 3. Normalized time-resolved emission spectra ($\lambda_{exc} = 445$ nm) of the catalysts **1a-b** and **2a-b** (50 μ M) in the presence of 0.2 M 1-phenylethanol (**3**) as quencher in acetonitrile under air.

In addition, the reduction potential of the excited state of the new catalysts **2** was estimated by combining cyclic-voltammetry and spectroscopic data.^[6] Despite the lower reduction potential of **2a** and **2b** ground states compared to **1a** and **1b**, the two imide-

based catalysts showed a comparable excited state reduction potential with **1a** and, to our delight, higher than the 9-mesityl derivative **1b** (see Table 1).

Further insight into the nature of the reactive excited states of **2a** or **1b** was obtained from CASPT2/CASSCF calculations (see Figure 4 and S.I. for more details). Regarding the Fukuzumi's catalyst **1b**, the calculations asserted the proposal previously inferred from the experimental data (Figure 4, left). Therefore, two excited species LE^{S_1} (localized, S_1) and CT^{S_2} (charge transfer, S_2) very close in energy (0.3 eV) were calculated at Franck Condon region, with oscillator strengths amounting to 0.1397 and 0.0068, respectively, indicating much higher absorption for LE^{S_1} than for CT^{S_2} . The geometry optimization of these excited states resulted in two new S_1 minima close in energy (CT^{S_1-min} and LE^{S_1-min} , 2.62 and 2.49 eV, respectively), with the localized species being slightly more stable (Figure 4).

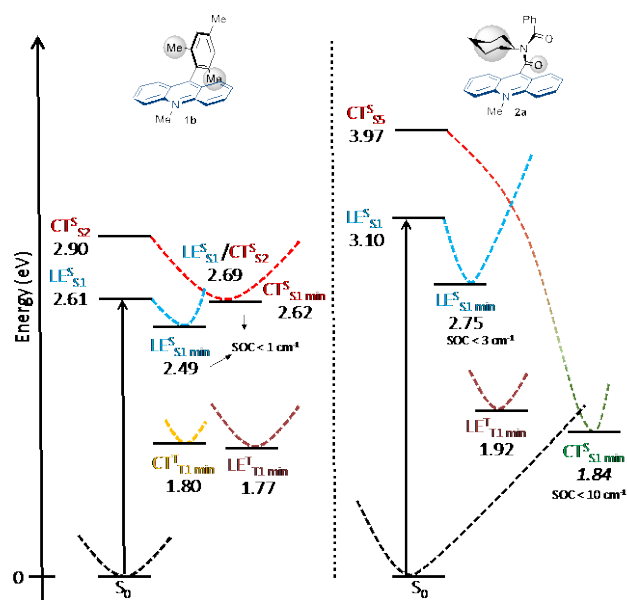


Figure 4. CASPT2/ANO-S//TD-M062X/6-31G* gas phase potential energy profiles for **1b** and **2a**. Energies relative to the S_0 in eV and spin-orbit couplings in cm^{-1} .

Our calculations also revealed that the CT^{S_2}/LE^{S_1} internal conversion funnel lies close to the two optimized minima. This translates into an almost negligible energy barrier interconnecting both the excited localized and charge transfer species, which is in agreement with the previously reported equilibrium between LE and CT species from experimental data.^[9b] The very small spin orbit coupling (< 1 cm^{-1}) calculated at the two S_1 minima also points to a small probability of population transfer to the triplet manifold, where the stability order of the CT^T and LE^T minima is maintained. Here, still the localized and CT triplet minima present similar energies (1.77 and 1.80 eV). Therefore, these data are fully consistent with the scenario describing an equilibrium between the LE and CT singlet excited minima, being the former species the active one, with the latter corresponding to a CT unproductive intermediate.

In contrast, the replacement of the mesityl by the imide group at the C-9 position results in a considerable destabilization of the CT electronic excited species, delocalized between the acridinium and phenyl moieties (Figure 4, right). In fact, the energy difference between the two states at the Franck Condon region amounts to 0.87 eV in the gas phase. The optimization of the localized excited state leads to a minimum with an energy of 2.75 eV relative to the ground state. The lowest lying CT state (S_5) at Franck Condon region evolves to a very stable CT minimum of different character, delocalized over the acridinium and imide moieties. The probability of transferring population to the triplet manifold from the LE minimum is predicted to be small ($SOC < 3 \text{ cm}^{-1}$). The couplings of the most stable CT state at the position of the minimum $CT^{S_{5min}}$ are however not negligible ($SOC \text{ ca. } 10 \text{ cm}^{-1}$ with the T_1). Still, the chances to leak population to the triplet manifold are small considering that the barrier to indirectly access the $CT^{S_{5min}}$ from $LE^{S_{5min}}$ is very large. Therefore, the larger energy barrier of **2** compared to **1** interconnecting the LE and CT minima makes the imide derivative a more active and efficient photocatalyst.

In conclusion, the herein studied novel class of photoredox catalysts **2** have showed the tendency of forming LE species, being CT states quite inaccessible, whereas in **1b** these CT and LE species are equally accessible. Considering that CT states are unproductive species in the catalytic system, our observations explain the better performances observed for **2a** and **2b** compared to the widely used 9-mesityl acridinium salt catalyst **1b**.

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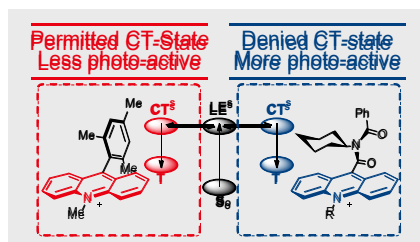
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COMMUNICATION

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