ChemCatChem
Concept
doi.org/10.1002/cctc.202500247
Chemistry Europe
European Chemical Societies Publishing
www.chemcatchem.org

Light-Driven CO_2 Reduction Catalysis with Organic Thermally Activated Delayed Fluorescence (TADF) Sensitizers

Federico Droghetti,[a] Andrea Mantovani,[a] and Mirco Natali*[a]

Catalytic conversion of CO_2 into carbon-based products (CO_2 reduction reaction, CO_2RR) using light can be profitably achieved through the merging of a molecular catalyst based on redox-active metals, a light-harvesting sensitizer, and an electron donor. Within this framework, the discovery of novel chromophores represents a critical task. Cyanoarenes are thermally-activated delayed fluorescence (TADF) dyes that have been largely considered as photoactive components in the field of lighting and organic photocatalysis. Only recently they have been also successfully employed as photosensitizers in light-driven CO_2RR schemes. While their application in lieu of more classical inorganic or organometallic chromophores might seem straightforward, several open points are still present concerning, e.g., mechanistic aspects and stability issues. This Concept aims to collect the most recent studies dealing with the application of these TADF dyes in combination with molecular complexes catalyzing the CO_2RR mainly to CO and/or formate, trying to highlight the most promising molecular scaffolds and identify possible misconceptions.

1. Introduction

The production of fuels or industrially relevant intermediates via the chemical conversion of CO_2 into reduced-carbon forms (CO_2 reduction reaction, CO_2RR) currently represents one of the main targets for scientists and researchers working in the field of artificial photosynthesis (AP).[1–5] In fact, this poses a challenging solution to the global issues associated with the continuous consumption of fossil fuels, such as global warming and climate change.[6] The one-electron reduction of CO_2 to its radical anion (Equation 1), while feasible, is highly energy-demanding.[4] On the other hand, smooth conversion of CO_2 into chemical fuels can be in principle achieved in the presence of a suitable proton donor, e.g., according to the reactions in Equations (2)–(6). However, since these reactions involve multiple electron and proton transfer steps, efficient and selective formation of carbon-based products is hampered by the complex mechanistic requirements, the possible competition among the different reactions (Equations 2–6) and the possible occurrence of the parallel, unwanted hydrogen evolving reaction (HER, Equation 7).

$$CO_2 + e^- \rightarrow CO_2^{\bullet -} \tag{1}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \tag{2}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \tag{3}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow H_2CO + H_2O \tag{4}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \tag{5}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \tag{6}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{7}$$

For all these reasons, the discovery of active and selective catalysts appears as a crucial task in the realm of CO_2RR. Inspired by the structural and functional motifs of the active sites of natural hydrogenases,[7–9] many molecular catalysts based on transition metal complexes have been conceived in the last years for this purpose mainly resulting in the effective generation of two-electron-reduced products (Equations 2 and 3). Among these, rhenium and ruthenium polypyridine complexes[10–17] as well as complexes based on Earth-abundant metals[18–29] have been profitably employed. Examples of this latter include, among others, porphyrins or polypyridine complexes of cobalt and iron.[30–43] In this respect, particular emphasis has been given to the use of redox non-innocent ligands which have proven to be extremely effective in targeting the selective reduction of CO_2 into CO by disfavoring the hydride pathway.[42–45]

The profitable conversion of CO_2 into a certain product is always an uphill reaction and as such requires the exploitation of a suitable energy source. For this purpose, solar energy can be considered one of the most sustainable solutions as it is clean, reliable, and abundant. To achieve light-driven conversion of CO_2 a minimum set of three components is however necessary: a catalyst (C), a photosensitizer (PS), and an electron donor

---

[a] F. Droghetti, A. Mantovani, M. Natali
Department of Chemical, Pharmaceutical and Agricultural Sciences (DOCPAS), University of Ferrara, Via L. Borsari 46, Ferrara 44121, Italy
E-mail: mirco.natali@unife.it

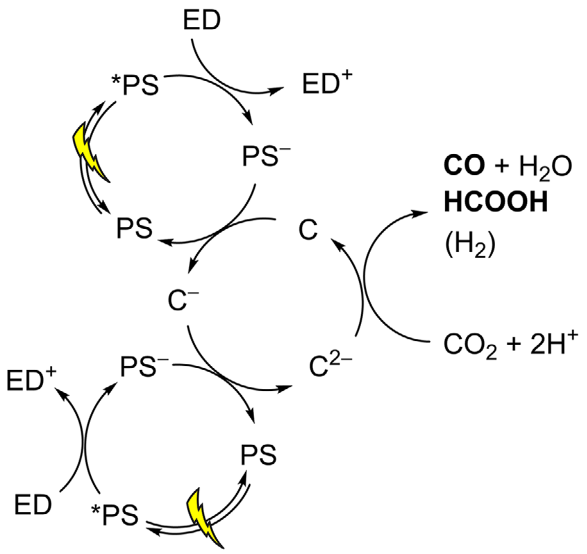

Figure 1. Schematic representation of the light-driven processes in a three-component system for the CO_2RR to two-electron reduced products; PS = photosensitizer, C = catalyst, ED = electron donor; chemical steps associated with the catalyst are herein neglected for simplicity reasons.

(ED).[9] According to the reaction scheme of Figure 1, CO_2RR into CO or formate (and the parallel HER) can occur in the presence of a proton donor upon excitation of the PS which, at the excited state level (*PS), can react with the ED leading to the formation of the reduced sensitizer species (PS$^-$). Subsequent electron transfers from the latter to the catalyst, in its initial (C) or one-electron reduced (C$^-$) forms lead to activation of the CO_2 substrate (or protons) and the resulting product formation. Within this reaction scheme, the choice of the PS is of pivotal relevance. As a matter of fact, the PS must efficiently absorb visible light, it has to possess an oxidation potential in its excited state sufficiently positive to react with the ED and a reduction potential in its ground state negative enough to effectively reduce the catalyst. Furthermore, since the primary photochemical step is the reaction between the excited PS* and the ED, a long excited-state lifetime is also required to allow an efficient bimolecular process.[46,47] For all these reasons, inorganic and organometallic complexes of ruthenium(II) and iridium(III), characterized by long-lived triplet metal-to-ligand charge transfer (MLCT) states, have been frequently considered as the prototype PSs.[41–43,45] However, they are based on rare and expensive metals, thus precluding extensive applications.

In the quest for alternative PSs, organic compounds have also been considered.[48,49] However, limited intersystem crossing (ISC) yields can be encountered in these latter,[50] leading to an inefficient population of the triplet excited state which is commonly involved in the primary photochemical process with the ED.[51,52] Moreover, the typically large singlet-triplet energy gap of common organic chromophores can impact on both the light-harvesting ability in the visible spectral range (associated with the population of the higher-energy singlet excited state) as well as on the resulting excited-state redox potentials.[53]

Cyanoarene dyes, characterized by thermally-activated delayed fluorescence (TADF), have recently emerged as promising PSs for light-driven catalysis, offering long-lived triplet excited states and small singlet-triplet energy gaps in a fully organic compound. Though already known and

Federico Droghetti (born 1996) received his PhD in Chemical Sciences at the University of Ferrara in February 2025. Currently, he is holding a post-doctoral fellowship at the same university under the supervision of Prof. M. Natali. His research interests are in the field of inorganic and coordination chemistry, with particular focus on CO_2 reduction catalysis

Andrea Mantovani (born 2000) graduated in Chemical Sciences in 2024 at the University of Ferrara. He is currently pursuing his PhD in Chemical Sciences under the supervision of Prof. M. Natali. His research interests are in the field of inorganic chemistry, light-driven catalysis, and photoelectrochemistry.

Mirco Natali (born 1986) is Associate Professor of General and Inorganic Chemistry at the Department of Chemical, Pharmaceutical and Agricultural Sciences (DOCPAS) of the University of Ferrara (Ferrara, Italy) since 2019. In 2014 he received his PhD in Chemical Sciences from the University of Ferrara under the guidance of Prof. Franco Scandola. His research interests deal with the light-driven catalysis of small molecule activation and the time-resolved spectroscopic characterization of molecular systems and nanomaterials for applications in photochemistry.

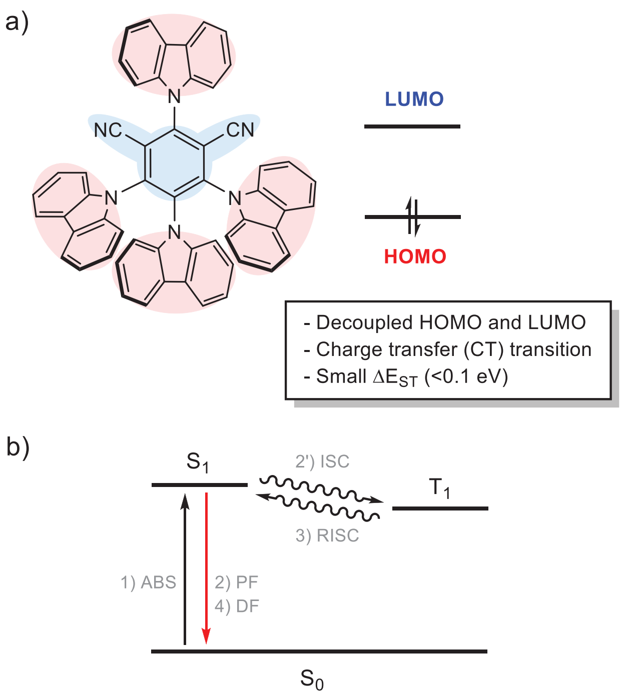

Figure 2. (a) Relevant electronic characteristics of cyanoarene dyes and (b) simplified Jablonski diagram showing the chronological sequence of photophysical steps characteristic of TADF (ABS = absorption, PF = prompt fluorescence, ISC = intersystem crossing, RISC = reverse intersystem crossing, DF = delayed fluorescence).

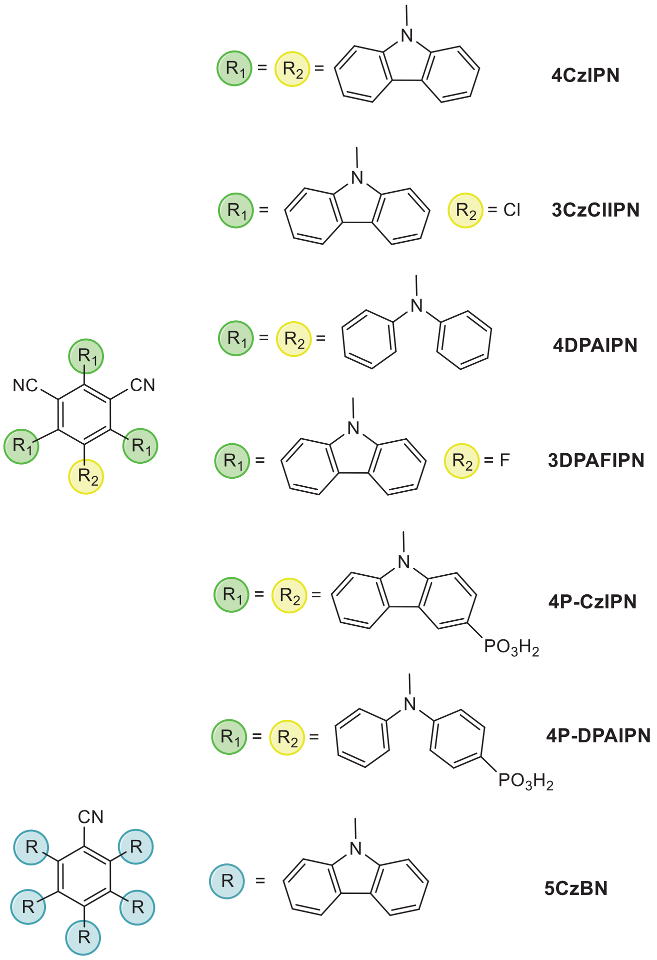

Figure 3. Molecular structures of the TADF dyes employed in light-driven CO_2RR studies.

employed both in the field of lighting devices[54] and organic photocatalysis,[53,55–57] their application in CO_2RR has only recently been explored. Hence, this Concept aims to highlight some recent findings connected with the application of cyanoarenes in light-driven catalysis of the CO_2RR, pointing out the main results as well as some open points.

2. Light-Driven CO_2RR with TADF Dyes

2.1. Photophysical Properties of TADF Dyes

Organic TADF dyes of the cyanoarene family can be easily prepared according to well-established methodologies.[53,58,59] Differently from common organic and organometallic compounds, they are generally characterized by highly twisted electron donating and accepting units which provide substantial electronic decoupling between the HOMO and LUMO orbitals (Figure 2a).[53] Under these conditions, a small energy gap originates between the first singlet and triplet excited states ($\Delta E < 0.1$ eV) resulting from a HOMO→LUMO charge transfer (CT) transition.

This represents a key motif at the basis of the peculiar photophysical behavior (Figure 2b). Spin-allowed excitation of the dye in its singlet excited state is usually followed by a favorable radiative decay to the ground state, known as prompt fluorescence (PF), featuring a lifetime in the order of ns characteristic of classical organic chromophores. ISC can, however, occur in competition with PF leading to the population of the triplet excited state. The decay of this latter to the ground state is usually slow due to the spin-forbidden nature of the transition. On the other hand, due to the small singlet-triplet energy gap, reverse intersystem crossing (RISC) from the T_1 to S_1 can efficiently take place at room temperature, resulting in an additional fluorescence component, known as delayed fluorescence (DF) and showing a lifetime in the order of µs. Furthermore, since the HOMO and the LUMO orbitals are located in different positions of the molecule, chemical modification can be easily exploited[53] to prepare different TADF dyes featuring specific absorption properties and redox potentials both at the ground and excited state level.

Figure 3 displays the molecular structures of the organic TADF dyes employed in light-driven CO_2RR, while the corresponding relevant photophysical and electrochemical parameters are collected in Table 1. All these dyes have, in principle, the basic requirements to be employed in light-driven catalytic cycles (Figure 1). They indeed display considerably long-lived DF and sufficiently positive oxidation potentials in the excited state rendering possible the bimolecular reaction with most electron donors both at the thermodynamic and kinetic level.[60] Furthermore, they are characterized by ground-state reduction potentials which are negative enough to activate many molecular catalysts toward the CO_2RR. Figure 4 depicts the metal

Table 1. Summary of the main photophysical and electrochemical properties of the organic TADF dyes employed in light-driven CO_2RR studies.

PS	τ_{PF}/ns[a]	τ_{DF}/μs[a]	E^*_{ox}/V[b),c)]	E^{red}/V[b),d)]
4CzIPN	21	2.1	+1.03	−1.72
3CzClIPN	13	32	+0.89	−1.61
4DPAIPN	2.9	84	+0.36	−2.08
3DPAFIPN	3.6	43	+0.69	−1.94
5CzBN	24	10	+0.91	−1.99
4P-CzIPN	26.8	1.5	+1.00	−1.62
4P-DPAIPN	2.6	36.2	+0.58	−1.94

[a] measured in *N,N*-dimethylacetamide (DMA) as the solvent.
[b] Potentials are referenced versus Fc^+/Fc.
[c] Values useful to evaluate the reactivity of the excited state with the ED.
[d] Values useful to evaluate the reactivity of the photogenerated reduced dye with the catalyst.

complexes employed as catalysts for the light-driven CO_2RR together with the TADF dyes.

2.2. Light-Driven CO_2RR

The first report in which an organic TADF dye was employed for the light-driven CO_2RR deals with the use of **4CzIPN** as the sensitizer in combination with triethylamine (TEA) as the sacrificial electron donor and the iron complex **Fe1** as the catalyst (Figure 4).[61] Visible-light irradiation of a solution containing 0.28 M TEA, 100 μM **4CzIPN**, and 10 μM **Fe1** in CO_2-saturated DMF delivered 12.3 μmol CO after 3 h of irradiation, corresponding to a maximum turnover number (TON) of 246. Optimization of the photocatalytic activity was obtained in the presence of H_2O as the proton donor, leading to a maximum TON of 2250 when photocatalysis was performed in a 3:2 DMF:H_2O mixture. Under these conditions, the generation of CO is attained with a quantum yield of 1%[62,63] and is practically quantitative with a selectivity of ca 99%. Highly selective generation of CO was also obtained using **4CzIPN** in combination with the iron complex **Fe2** (Figure 4).[64] Under optimized conditions (10 μM **Fe1**, 0.3 mM **4CzIPN**, 0.28 M TEA in 4:1 DMF:H_2O under CO_2), CO is produced with a maximum TON of 878, while only traces of H_2 were detected.

In a subsequent report, Chao and co-workers employed **4CzIPN** as the sensitizer with the ruthenium complex **Ru1** (Figure 4).[65] Generation of CO (14 μmol, corresponding to a maximum TON of 124) with a quantum yield of 0.14%[62,63] and a selectivity of 96.5% was obtained following irradiation of a 4:1 acetonitrile:H_2O solution containing 20 μM **Ru1**, 0.1 mM **4CzIPN**, and 0.28 TEA. In a similar manner, the photoproduction of CO (18.4 μmol, TON = 41) with a selectivity of 94% was attained using **4CzIPN** and TEA in combination with the nickel complex **Ni1** (Figure 4) as the CO_2RR catalyst.[66]

Remarkably, the light-driven catalytic activity by both **Ru1** and **Ni1** was restricted to the cyanoarene dye, since almost negligible activity was observed for both complexes using either $[Ru(bpy)_3]^{2+}$ (where bpy = 2,2′-bipyridine) or $[Ir(ppy)_3]$ (where ppy = 2-phenylpyridine) as the sensitizer.[65,66] The authors rationalized this experimental evidence proposing the occurrence of a consecutive photoinduced electron transfer (ConPET) mechanism using **4CzIPN**. This process would involve the excitation of the dye, the reductive quenching by the TEA electron donor, and the subsequent excitation of the resulting radical anion **4CzIPN**$^{\bullet-}$ (Figure 5a). This would generate the excited state ***4CzIPN**$^{\bullet-}$ acting as a powerful reductant toward catalyst acti-

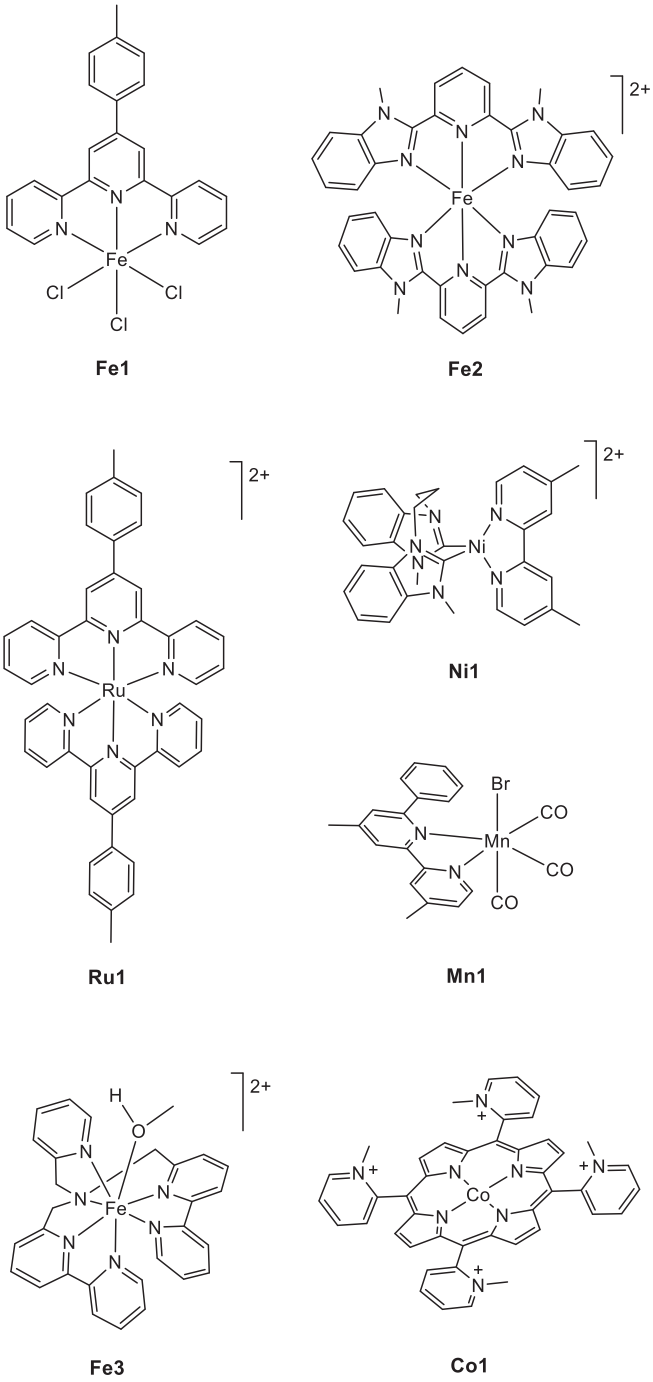

Figure 4. Structures of the molecular catalysts employed in light-driven CO_2RR studies in combination with TADF dyes.

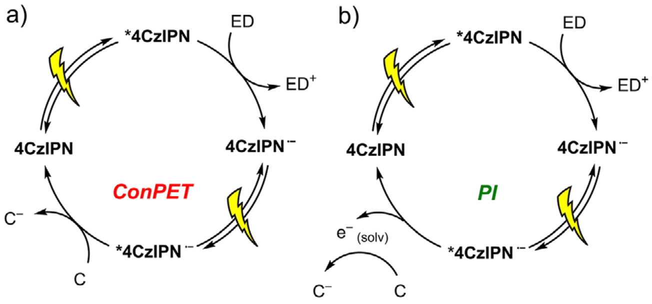

Figure 5. Two-photon processes potentially leading to catalyst activation occurring using **4CzIPN** in the presence of an electron donor: (a) consecutive photoinduced electron transfer (ConPET), proposed by Chao and co-workers[65] and (b) two-photon photoionization (PI), reported by Ceroni and co-workers.[67] Legend: ED = electron donor, C = catalyst (only the first electron transfer is herein considered for simplicity).

vation, even stronger than the one-electron reduced species of the inorganic sensitizers, thus explaining the superior activity.

A careful reexamination of this hypothesis, however, definitely suggests alternative possibilities. As a matter of fact, the ConPET process is a two-photon process and is intrinsically unlikely under conventional irradiation conditions as it involves a photogenerated intermediate, whose concentration is expected to be small under steady-state irradiation. This notwithstanding, Ceroni and co-workers recently demonstrated by time-resolved ultrafast spectroscopy that excitation of the radical anion **4CzIPN**$^{\bullet-}$ is followed by photoionization,[67] resulting in the generation of solvated electrons (Figure 5b). Hence, if a two-photon process were operative under continuous photolysis conditions, reductive activation of the catalyst would be expected to involve solvated electrons and not the excited state of the radical anion.

Furthermore, the possible role of carbon-based radical species generated upon photo triggered oxidation of the TEA electron donor by the excited state of the sensitizer and subsequent deprotonation is fully neglected.[60,68] In this respect, the more positive excited state oxidation potential of **4CzIPN** than both $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_3]$ could be consistent with a more effective generation of such radical species. More importantly, upon continuous irradiation of **4CzIPN** in the presence of TEA, the development of a new emission band was observed featuring a lifetime in the order of µs, which was ascribed to the luminescence of the **4CzIPN**$^{\bullet-}$ radical anion.[65] However, an excited doublet state like ***4CzIPN**$^{\bullet-}$, if produced, would be expected to be extremely short-lived and thus non-luminescent.[69] Accordingly, these results suggest that photoreaction between **4CzIPN** and TEA might instead lead to some additional photoproduct, likely maintaining a structural similarity with the original TADF dye. This species could display different photophysical and electrochemical properties than the pristine **4CzIPN** resulting in a different reactivity within the catalytic cycle of Figure 1 involving TEA and **Ru1** or **Ni1**. Chemical modification of **4CzIPN** under photocatalytic conditions has been indeed already documented by König and co-workers.[70,71]

The TADF dyes **4CzIPN**, **3CzClIPN**, **5CzBN**, **3DPAFIPN**, and **4DPAIPN** were tested by Ceroni, Ishitani, and co-workers as light-harvesting sensitizers in combination with the manganese complex **Mn1** (Figure 4) as the catalyst and 1,3-dimethyl-2-phenylbenzimidazoline (BIH) as the sacrificial electron donor in triethanolamine (TEOA) / *N*,*N*-dimethylacetamide (DMA) mixture.[72] The negligible activity was recorded using **4CzIPN** and **3CzClIPN**, ascribed to the poor reducing ability of the photogenerated PS^- species within the reaction mechanism of Figure 1. Some CO and formate (3.1 and 1.1 µmol, respectively) were detected instead when photocatalysis was attempted using **5CzBN**, thanks to the more negative reduction potential than the previous dyes. However, a substantial generation of photoproducts was only achieved using both **3DPAFIPN** and **4DPAIPN**. Under optimized conditions (5:1 PS:C ratio and irradiation at 440 nm), **3DPAFIPN** delivers 53.8 µmol CO, 18.9 µmol HCOOH, and 2.9 µmol H_2 after 20 h, leading to maximum TONs of 538, 130, and 55, respectively. On the other hand, **4DPAIPN** generates 47.6 µmol CO, 18.9 µmol HCOOH, and 2.9 µmol H_2 after 20 h (1:1 PS:C ratio and irradiation at 470 nm) corresponding to maximum TONs of 476, 189, and 29, respectively. For this latter, a quantum yield of 22.8% was recorded for the generation of reduced carbon products (i.e., CO + HCOOH). Overall, the results reported highlight how efficient photocatalytic activity using the manganese complex **Mn1** can be achieved by taking advantage of organic TADF dyes exhibiting high molar absorption coefficients in the visible and sufficiently negative reduction potentials.[72]

More recently, the TADF dyes **4CzIPN**, **3DPFIPN**, and **4DPAIPN** were considered for light-driven CO_2RR by the heptacoordinated iron complex **Fe3** (Figure 4),[73] whose catalytic activity was previously demonstrated using the $[Ru(bpy)_3]^{2+}$ sensitizer.[42,43] Experiments were conducted in acetonitrile solution using *N*,*N*-diisopropylethylamine (DIPEA) as the electron donor and 2,2,2-trifluoroethanol (TFE) as the proton donor under 1 sun (0.1 $W{\cdot}cm^{-2}$) irradiation.[73] Limited activity was observed using **3DPFIPN**, associated with a rapid bleaching of the solution. Substantial formation of CO (127 µmol after 7 h, corresponding to a maximum TON of 508) with a selectivity of 99% was instead recorded using **4CzIPN** as the sensitizer. However, a noticeable lag phase was detected in the generation of CO and a neat change in the absorption spectrum was apparent when the photoreaction was stopped. Both these evidences may suggest a degradation pathway involving **4CzIPN** with the resulting light-driven catalysis occurring through the intermediacy of a new PS species.[70,71] These results nicely support the hypothesis previously discussed and highlight the relevance of a detailed mechanistic understanding of light-driven catalysis.

Efficient formation of CO with catalyst **Fe3** (278 µmol after 7 h of irradiation, corresponding to a maximum TON of 1112) was obtained using **4DPAIPN** as the sensitizer. More importantly, the photochemical activity with this dye was solely limited by the degradation of the catalyst, pointing out the great stability of the sensitizer. For this photosystem, a selectivity >99% and an outstanding quantum yield of 36% for CO formation were registered.[73] Transient absorption spectroscopy measurements confirmed that the observed remarkable performances can be attributed to the fast kinetics associated with the electron transfer from the photogenerated reduced sensitizer to the iron catalyst which is instrumental to promoting efficient catalysis while preserving the sensitizer from parallel, detrimental degradation pathways. These results well comply with those previously obtained with the **Mn1** catalyst,[72] highlighting how the merging of **4DPAIPN** and Earth-abundant metal catalysts can be fruitfully exploited to efficiently convert CO_2 into carbon-based products.

The light-driven catalytic studies discussed so far have been conducted in organic solvents (DMF, DMA, or acetonitrile), due to the good solubility of cyanoarene dyes in such media. Moving toward an aqueous environment to accomplish the CO_2RR represents an ideal solution in the green chemistry context. For this reason, Ouyang and co-workers purposely designed and synthesized the water-soluble TADF dyes **4P-CzIPN** and **4P-DPAIPN** featuring phosphonic acid groups (Figure 3).[74] These dyes were tested as PSs in combination with the cobalt porphyrin **Co1** as the catalyst (Figure 4) and ascorbate as the sacrificial electron donor in $NaHCO_3$ aqueous buffer solution at pH 6.7. Under these conditions, while negligible activity was observed using **4P-CzIPN**, the formation of CO with a maximum TON of 2700 after 20 h of visible-light irradiation and a selectivity of 92.5% was obtained using **4P-DPAIPN**. Remarkably, almost negligible degradation of the organic dye was observed after photocatalysis, highlighting the great stability of the **4DPAIPN** scaffold both in organic and aqueous media.[73,74]

3. Summary and Outlook

In this Concept, we have described the most recent examples where organic TADF dyes have been employed as sensitizers within light-driven catalytic schemes for the CO_2RR into CO and/or formate in combination with molecular catalysts. Overall, the results suggest that this class of chromophores can play a leading role even in this research field allowing the replacement of common inorganic and organometallic sensitizers usually based on noble metals such as ruthenium and iridium. Nonetheless, their application must take into account stability issues, as the tendency to degrade or convert into different active species[70,71] is often overlooked. In this regard, while complementary studies suggest that **4DPAIPN** (or its water-soluble derivative) can be identified as the most active and stable TADF dye toward light-driven CO_2RR, the poor activity of the remaining sensitizers studied and the controversial results obtained with **4CzIPN** definitely demonstrate that much room for improvement still exists. Furthermore, it is important to highlight that a detailed mechanistic understanding of the photoinduced dynamics within the light-driven reaction schemes involving cyanoarene dyes is imperative to recognize the actual role of the sensitizer as well as potential degradation pathways. Only through these joint efforts the discovery of novel and more effective photosensitizers will be possible.

Acknowledgements

Financial support from the Italian MUR (PRIN2020, Electrolight4Value, 2020927WY3), the European Union – Next Generation EU (PRIN2022 PNRR PHOTOCORE, P2022ZSPWF), and the University of Ferrara (FAR2024) are gratefully acknowledged.

Open access publishing facilitated by Universita degli Studi di Ferrara, as part of the Wiley - CRUI-CARE agreement.

Conflict of Interests

The authors declare no conflict of interest.

Keywords: CO_2 reduction · Cyanoarene · Homogeneous catalysis · Photosensitizer · Thermally-activated delayed fluorescence

[1] A. Morris, G. J. Meyer, E. Fujita, *Acc. Chem. Rev.* **2009**, *42*, 1983–1994.
[2] J. L. White, M. F. Baruch, J. E. Pander III, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.* **2015**, *115*, 12888–12935.
[3] H. Takeda, C. Cometto, O. Ishitani, M. Robert, *ACS Catal.* **2017**, *7*, 70–88.
[4] E. E. Benson, C. P. Kubiak, A. Sathrum, J. M. Smieja, *Chem. Soc. Rev.* **2009**, *38*, 89–99.
[5] A. Goeppert, M. Czaun, J. P. Jones, G. K. Surya Prakash, G. A. Olah, *Chem. Soc. Rev.* **2014**, *43*, 7995–8048.
[6] J. R. Norris, R. J. Allen, A. T. Evan, M. D. Zelinka, C. W. O'Dell, S. A. Klein, *Nature* **2016**, *536*, 72–75.
[7] W. Lubitz, H. Ogata, O. Rüdiger, E. Reijerse, *Chem. Rev.* **2014**, *114*, 4081–4148.
[8] M. Can, F. A. Armstrong, S. W. Ragsdale, *Chem. Rev.* **2014**, *114*, 4149–4174.
[9] F. Droghetti, A. Amati, A. Ruggi, M. Natali, *Chem. Commun.* **2024**, *60*, 658–673.
[10] H. Takeda, K. Koike, H. Inoue, O. Ishitani, *J. Am. Chem. Soc.* **2008**, *130*, 2023–2031.
[11] T. Nakajima, Y. Tamaki, K. Ueno, E. Kato, T. Nishikawa, K. Ohkubo, Y. Yamazaki, T. Morimoto, O. Ishitani, *J. Am. Chem. Soc.* **2016**, *138*, 13818–13821.
[12] J. M. Smeja, C. P. Kubiak, *Inorg. Chem.* **2010**, *49*, 9283–9289.
[13] J. A. Keith, K. A. Grice, C. P. Kubiak, E. A. Carter, *J. Am. Chem. Soc.* **2013**, *135*, 15823–15829.
[14] R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani, K. Maeda, *J. Am. Chem. Soc.* **2016**, *138*, 5159–5170.
[15] P. Kang, Z. Chen, A. Nayak, S. Zhang, T. J. Meyer, *Energy Environ. Sci.* **2014**, *7*, 4007–4012.
[16] S. Gonell, E. A. Assaf, K. D. Duffee, C. K. Schauer, A. J. M. Miller, *J. Am. Chem. Soc.* **2020**, *142*, 8980–8999.
[17] B. A. Johnson, S. Maji, H. Agarwala, T. A. White, E. Mijangos, S. Ott, *Angew. Chem., Int. Ed.* **2016**, *55*, 1825–1829.
[18] M. D. Sampson, A. D. Nguyen, K. A. Grice, C. E. Moore, A. L. Rheingold, C. P. Kubiak, *J. Am. Chem. Soc.* **2014**, *136*, 5460–5471.
[19] M. D. Sampson, C. P. Kubiak, *J. Am. Chem. Soc.* **2016**, *138*, 1386–1393.
[20] F. Franco, M. F. Pinto, B. Royo, J. Lloret-Fillol, *Angew. Chem., Int. Ed.* **2018**, *57*, 4603–4606.
[21] B. Reuillard, K. H. Ly, T. E. Rosser, M. F. Kuehnel, I. Zebger, E. Reisner, *J. Am. Chem. Soc.* **2017**, *139*, 14425–14436.
[22] S. Gonell, J. Lloret-Fillol, A. J. M. Miller, *ACS Catal.* **2021**, *11*, 615–626.
[23] R. Bonetto, R. Altieri, M. Tagliapietra, A. Barbon, M. Bonchio, M. Robert, A. Sartorel, *ChemSusChem* **2020**, *13*, 4111–4120.
[24] L. L. Gracia, E. Barani, J. Braun, A. B. Carter, O. Fuhr, A. K. Powell, K. Fink, C. Bizzarri, *ChemCatChem* **2022**, *14*, e202201163.
[25] S. L. Hooe, J. M. Dressel, D. A. Dickie, C. W. Machan, *ACS Catal.* **2020**, *10*, 1146–1151.
[26] K. Kosugi, H. Kashima, M. Kondo, S. Masaoka, *Chem. Commun.* **2022**, *58*, 2975–2978.
[27] A. W. Nichols, S. L. Hooe, J. S. Kuehner, D. A. Dickie, C. W. Machan, *Inorg. Chem.* **2020**, *59*, 5854–5864.
[28] W. Nie, D. E. Tarnopol, C. C. L. McCrory, *J. Am. Chem. Soc.* **2021**, *143*, 3764–3778.
[29] D. Hong, T. Kawanishi, Y. Tsukakoshi, H. Kotani, T. Ishizuka, T. Kojima, *J. Am. Chem. Soc.* **2019**, *141*, 20309–20317.

[30] Z. Guo, G. Chen, C. Cometto, B. Ma, H. Zhao, T. Groizard, L. Chen, H. Fan, W. L. Man, S. M. You, K. C. Lau, T. C. Lau, M. Robert, *Nat. Catal.* **2019**, *2*, 801–808.

[31] L. Chen, Z. Guo, X. G. Wei, C. Gallenkamp, J. Bonin, E. Anxolabéhère-Mallart, K. C. Lau, T. C. Lau, M. Robert, *J. Am. Chem. Soc.* **2015**, *137*, 10918–10921.

[32] X. Zhang, M. Cibian, A. Call, K. Yamauchi, K. Sakai, *ACS Catal.* **2019**, *9*, 11263–11273.

[33] I. Azcarate, C. Constentin, M. Robert, J.-M. Savéant, *J. Am. Chem. Soc.* **2016**, *138*, 16639–16644.

[34] I. Azcarate, C. Constentin, M. Robert, J.-M. Savéant, *J. Phys. Chem. C* **2016**, *120*, 28951–28960.

[35] C. G. Margarit, N. G. Asimov, C. Constentin, D. G. Nocera, *ACS Energy Lett.* **2020**, *5*, 72–78.

[36] S. Amanullah, P. Saha, A. Dey, *J. Am. Chem. Soc.* **2021**, *143*, 13579–13592.

[37] D. Z. Zee, M. Nippe, A. E. King, C. J. Chang, J. R. Long, *Inorg. Chem.* **2020**, *59*, 5206–5217.

[38] W. Xia, Y. Y. Ren, J. Liu, B. Y. Deng, F. Wang, *J. Photochem. Photobio A: Chem.* **2022**, *426*, 113754.

[39] N. Elgrishi, M. B. Chambers, V. Artero, M. Fontecave, *Phys. Chem. Chem. Phys.* **2014**, *16*, 13635–13644.

[40] J.-S. Derrick, M. Loipersberger, R. Chatterjee, D. A. Iovan, P. T. Smith, K. Chakarawet, J. Yano, J. R. Long, M. Head-Gordon, C. J. Chang, *J. Am. Chem. Soc.* **2020**, *142*, 20489–20501.

[41] L. Duan, G. F. Manbeck, M. Kowalczyk, D. J. Szalda, J. T. Muckerman, Y. Himeda, E. Fujita, *Inorg. Chem.* **2016**, *55*, 4582–4594.

[42] F. Droghetti, A. Amati, F. Pascale, A. Crochet, M. Pastore, A. Ruggi, M. Natali, *ChemSusChem* **2024**, *17*, e202300737.

[43] F. Droghetti, F. Lemken, L. Rulisek, A. Ruggi, M. Natali, *ACS Catal.* **2024**, *14*, 16920–16935.

[44] N. Queyriaux, *ACS Catal.* **2021**, *11*, 4024–4035.

[45] P. De La Torre, J. S. Derrick, A. Snider, P. T. Smith, M. Loipersberger, M. Head-Gordon, C. J. Chang, *ACS Catal.* **2022**, *12*, 8484–8493.

[46] E. S. Andreiadis, M. Chavarot-Kerlidou, M. Fontecave, V. Artero, *Photochem. Photobio.* **2011**, *87*, 946–964.

[47] K. Ladomenou, M. Natali, E. Iengo, G. Charalampidis, F. Scandola, A. G. Coutsolelos, *Coord. Chem. Rev.* **2015**, *304–305*, 38–54.

[48] M. Kientz, G. Lowe, B. G. McCarthy, G. M. Miyake, J. Bonin, M. Robert, *ChemPhotoChem* **2022**, *6*, e202200009.

[49] P. Y. Ho, S. C. Cheng, F. Yu, Y. Y. Yeung, W. X. Ni, C. C. Ko, C. F. Leung, T. C. Lau, M. Robert, *ACS Catal.* **2023**, *13*, 5979–5985.

[50] E. Bassan, A. Gualandi, P. G. Cozzi, P. Ceroni, *Chem. Sci.* **2021**, *12*, 6607–6628.

[51] T. M. McCormick, B. D. Calitree, A. Orchard, N. D. Kraut, F. V. Bright, M. R. Detty, R. Eisenberg, *J. Am. Chem. Soc.* **2010**, *132*, 15480–15483.

[52] M. Natali, R. Argazzi, C. Chiorboli, E. Iengo, F. Scandola, *Chem. - Eur. J.* **2013**, *19*, 9261–9271.

[53] A. Vega-Peñaloza, J. Mateos, X. Companyó, M. Escudero-Casao, L. Dell'Amico, *Angew. Chem., Int. Ed.* **2021**, *133*, 1096–1111.

[54] M. Y. Wong, E. Zysman-Colman, *Adv. Mater.* **2017**, *29*, 1605444.

[55] T. Y. Shang, L. H. Lu, Z. Cao, Y. Liu, W. M. He, B. Yu, *Chem. Commun.* **2019**, *55*, 5408–5419.

[56] P. P. Singh, V. Srivastava, *Org. Biomol. Chem.* **2021**, *19*, 313–321.

[57] M. A. Bryden, E. Zysman-Colman, *Chem. Soc. Rev.* **2021**, *50*, 7587–7680.

[58] S. M. Engle, T. R. Kirkner, C. B. Kelly, *Org. Synth.* **2019**, *96*, 455–473.

[59] E. Speckmeier, T. G. Fischer, K. Zeitler, *J. Am. Chem. Soc.* **2018**, *140*, 15353–15365.

[60] Y. Pellegrin, F. Odobel, *C. R. Chimie* **2017**, *20*, 283–295.

[61] Y. Wang, X. W. Gao, J. Li, D. Chao, *Chem. Commun.* **2020**, *56*, 12170–12173.

[62] The quantum yield has been recalculated considering that light-driven CO_2 conversion into CO using TEA as the sacrificial electron donor requires one photon instead of two (see ref. 56).

[63] H. Kumagai, Y. Tamaki, O. Ishitani, *Acc. Chem. Res.* **2022**, *55*, 978–990.

[64] T. Liu, L. Chen, D. Chao, *Dalton Trans.* **2022**, *51*, 4052–4057.

[65] Y. Fang, T. Liu, L. Chen, D. Chao, *Chem. Commun.* **2022**, *58*, 7972–7975.

[66] T. Liu, Y. Fang, Y. Li, Y. Fu, D. Chao, *J. Mol. Struct.* **2023**, *1277*, 134858.

[67] M. Villa, A. Fermi, F. Calogero, X. Wu, A. Gualandi, P. G. Cozzi, A. Troisi, B. Ventura, P. Ceroni, *Chem. Sci.* **2024**, *15*, 14739–14745.

[68] P. J. Delaive, T. K. Foreman, C. Giannotti, D. G. Whitten, *J. Am. Chem. Soc.* **1980**, *102*, 5627–5631.

[69] H. Li, O. Wenger, *Angew. Chem., Int. Ed.* **2022**, *61*, e202110491.

[70] K. Donabauer, M. Maity, A. L. Berger, G. S. Huff, S. Crespi, B. König, *Chem. Sci.* **2019**, *10*, 5162–5166.

[71] Q. Y. Meng, T. E. Schirmer, A. L. Berger, K. Donabauer, B. König, *J. Am. Chem. Soc.* **2019**, *141*, 11393–11397.

[72] E. Bassan, R. Inoue, D. Fabry, F. Calogero, S. Potenti, A. Gualandi, P. G. Cozzi, K. Kamagawa, P. Ceroni, Y. Tamaki, O. Ishitani, *Sustain. Energy Fuels* **2023**, *7*, 3454.

[73] F. Droghetti, L. Villa, A. Sartorel, L. Dell'Amico, A. Ruggi, M. Natali, *ChemSusChem* **2025**, *18*, e202402627.

[74] F. Ma, Z. M. Luo, J. W. Wang, G. Ouyang, *J. Am. Chem. Soc.* **2024**, *146*, 17773–17783.

Manuscript received: February 14, 2025
Revised manuscript received: March 13, 2025
Accepted manuscript online: March 17, 2025
Version of record online: ■■, ■■