**CH-π interaction boosts photocatalytic CO₂ reduction activity in a noble-metal-free system with a molecular cobalt catalyst anchored on carbon nitride**

Jia-Wei Wang,¹ Marcos Gil-Sepulcre,²,³ Hai-Hua Huang,⁴ Eduardo Solano,⁵ Yan-Fei Mu,⁶ Antoni Llobet*,²,³,10 Gangfeng Ouyang*,¹,7,8,9

¹KLGHEI of Environment and Energy Chemistry, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China

²Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology (BIST), 43007 Tarragona, Spain

³Departament de Química, Universitat Autònoma de Barcelona, 08193 Barcelona, Spain

⁴School of Materials Science & Engineering, School of Chemistry, PCFM Lab, Sun Yat-sen University, Guangzhou 510275, China

⁵NCD-SWEET beamline, ALBA synchrotron light source. Carrer de la Llum, 2, 26, 08290 Cerdanyola del Vallès, Barcelona

⁶Institute of New Energy Materials and Low Carbon Technology, School of Material Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

⁷Instrumental Analysis and Research Center, Sun Yat-sen University, Guangzhou, 510275, China

⁸Chemistry College, Center of Advanced Analysis and Gene Sequencing, Zhengzhou University, Zhengzhou 450001, China

⁹Guangdong Provincial Key Laboratory of Emergency Test for Dangerous Chemicals, Guangdong Institute of Analysis (China National Analytical Center Guangzhou), Guangzhou, 510070, China

¹⁰The Lead Contact

*Correspondence: allobet@iciq.cat (A. Llobet); cesoygf@mail.sysu.edu.cn (G. Ouyang)
Summary

The construction of efficient noble-metal-free systems for visible-light-driven CO₂ reduction still remains a key challenge. Here we report an efficient molecular hybrid system composed of a Co-PYN5 catalyst that contains a pyrene functionality that anchors on g-C₃N₄ dye surface via CH-π interactions. This hybrid material achieves high TONs and TOFs for visible light reduction of CO₂ to CO of 533 and 95 h⁻¹, that are within the best reported up to now. The exceptional performance is rationalized in terms of the electronic coupling that takes place with the π-system of the pyrene group with both the g-C₃N₄ surface and the Co-pyridyl moiety of the catalysts.
Introduction

The light induced transformation of CO$_2$ into reduced products such as CO, CH$_4$, MeOH, EtOH or others is of great interest because it can reduce the concentration of CO$_2$ in the atmosphere and thus mitigate the effects of global warming.\textsuperscript{1-3,4,5} Further, CO$_2$ reduced products can be used as synthons for the chemical industry to generate value-added chemicals.\textsuperscript{6-8}

Several first-row transition metal complexes have been identified so far as CO$_2$ reduction catalysts (CRCs) that are capable of catalytically reducing CO$_2$ with good efficiencies and certain degree of selectivity, although improvement is still needed to employ them for technological purposes. The well-defined redox properties and mechanistic understanding of molecular catalyst allow to obtain a valuable knowledge of the key factors that govern the overall catalytic performance.\textsuperscript{9,10} This in turn is the \textit{sine qua non} condition for the rational design of selective and powerful catalyst based on the molecular toolkit. The versatility of the latter constitutes an excellent platform for the discovery of long lasting, powerful and selective CO$_2$ reduction catalysts based on a judicious choice of transition metals and ligands.\textsuperscript{9,11}

Regarding the light induced reduction of CO$_2$, many examples described in the literature use precious metals like Re,\textsuperscript{12} Ru\textsuperscript{13-15} or Ir\textsuperscript{8,16} and only a limited number of them utilize organic dyes\textsuperscript{17,18} or abundant transition metal complexes\textsuperscript{19-21} as catalysts and/or photosensitizers. Recent efforts have been focused on the use of earth-abundant systems,\textsuperscript{22-25} but their performances are far from ideal and thus need substantial improvement. In this context, graphitic carbon nitride (g-C$_3$N$_4$) emerges as a very interesting material, due to its facile synthesis and easily tunable properties.\textsuperscript{25-31} Pioneering examples utilize Ru complexes with mesoporous g-C$_3$N$_4$ (mpg-g-C$_3$N$_4$) to achieve visible-light-driven CO$_2$ reduction to HCOOH with high selectivity\textsuperscript{29,30,32,33} and recently, a carbon nitride/Fe-qpy (qpy is 2,2':6',2''-quaterpyridine) system was reported to exhibit an impressive TON of 155 and 97% selectivity for the generation of CO.\textsuperscript{27}

Several factors are fundamental for the successful accomplishment of light induced CO$_2$ reduction using solid state molecular hybrid materials. These include the intrinsic capacity of the CO$_2$ reduction molecular catalyst to effectively and selectively transform CO$_2$ to CO (or other reduced products) at relatively low overpotentials and the use of a light absorbing material with the right band energies and a sufficiently long charge separation state that can effectively interact with the
molecular catalysts. The nature and degree of the interaction of the material with the molecular catalyst will be determined by the electronic communication between them that in turn will affect the interfacial electron transfer kinetics and therefore is one of the crucial elements for a successful design of a solid-state light induced CO\textsubscript{2} reduction system.\textsuperscript{34,35}

In this regard, for the particular case of g-C\textsubscript{3}N\textsubscript{4}, several strategies have been used, including weak van der Waals interactions\textsuperscript{27} between molecular catalyst and g-C\textsubscript{3}N\textsubscript{4} as well as strong covalent amide bonds.\textsuperscript{24,36} In the latter case the amide bond is generated between free amine groups at the g-C\textsubscript{3}N\textsubscript{4} semiconductor and a non-bonding carboxylic group of the ligand bonded to a cobalt center. Further π-π stacking interaction have also been used in molecular catalysts by simply adding them on top of the g-C\textsubscript{3}N\textsubscript{4} surfaces or using a polymerization strategy.\textsuperscript{25,31}

![Figure 1. Catalyst structures.](image)

(a) Drawn structures for Co-N5 and Co-PYN5. (b) ORTEP plot of the cationic part of the complex [Co(PYN5)(MeCN)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2}. Color code: Co, green; N, blue; C, gray; H, white. Counter ions have been omitted for clarity.

To this end, we considered the utilization of a novel anchoring methodology based on CH-π interactions\textsuperscript{37-40} between the CH-aromatic groups of the ligand and the π-system of g-C\textsubscript{3}N\textsubscript{4} absorber as a simple strategy to prepare molecular hybrid materials that can potentially accelerate interfacial electron transfer via this type of bonding. For this purpose, we have prepared a Co complex that contains the ligand, (2E,12E)-2,13-dimethyl-14-(pyren-1-yl)-3,6,9,12-tetraaza-1(2,6)-pyridinacyclotricaphepane-2,12-diene, abbreviated as PYN5. The latter is a pentadentate ligand that occupies the equatorial positions of the Co metal center and that contains a pyrene group appended
into its pyridyl ring, as can be observed in **Figure 1**. Further, the PYN5 ligand coordinates the Co(II) center as a neutral ligand and hence enables the dicationic nature of the Co-PYN5 complex.

**Results and discussion**

Here on we report the synthesis and characterization of Co-PYN5, its anchoring onto g-C₃N₄, as well as the characterization of the new molecular hybrid material, Co-PYN5@g-C₃N₄. Further, we describe the performance of Co-PYN5@g-C₃N₄ regarding its capacity to catalytically carry out the light induced reduction of CO₂ to CO. The present system displays very high values in terms of both TON (533) and TOF (95 h⁻¹) for photocatalytic CO₂-to-CO conversion with organic absorbers and using first row transition metals as catalysts.

Further, it is the first example of anchoring a molecular catalyst via CH-π interaction for the CO₂ reduction reaction. For comparative purposes the parent Co complex without the appended pyrene group, Co-N5 (N5 is (2E,12E)-2,13-dimethyl-3,6,9,12-tetraaza-1(2,6)-pyridinacyclotridecaph-ane-2,12-diene; **Figure 1**) was also prepared. The synthesis of Co-N5 consists of a template complexation reaction where 2,6-diacetyl-pyridyl reacts with triethylenetetramine in the presence of Co(II) salts as previously described in the literature. A similar method was used for the synthesis of Co-PYN5 but using the diacetyl reactant functionalized with a pyrene moiety. This generates Co-PYN5 that is highly soluble in MeCN and crystallizes as the [Co(PYN5)(MeCN)₂](ClO₄)₂ complex where two solvent molecules coordinate to the Co metal center, as can be observed in the ORTEP structure shown in **Figure 1**. The metal center has a pseudo pentagonal bipyramidal geometry where the PYN5 ligand occupies the equatorial position while the MeCN ligand coordinated at the axial ones. It is interesting to realize here that the equatorial Co-N bonding distances range from 2.19 to 2.27 Å with an average of 2.24 Å. This is 0.30 Å larger than typical Co(II)-N bonds for related complexes such as Co-N4, [Co(N4)]²⁺ (N4 = (2E,12E)-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]hepta-deca-1(17),2,11,13,15-pentaene), which contains a tetradentate equatorial ligand and manifests that in Co-PYN5 the Co-N bonds at the equatorial zone are relatively weak and can synchronically coordinate and decoordinate in order not to violate the 18-electron rule. As a consequence, when one of the aliphatic N of PYN5 is not coordinated, it can also act as a proton acceptor or hydrogen bonding site close to the axial positions where the CO₂ reduction
transformation will occur and therefore can help to significantly reduce the activation energies for the CO$_2$ reduction reaction as has been recently reported for both reduction and oxidation reactions involving proton transfer steps in the rate determining step.$^{42,43}$ Another interesting feature of the [Co(PYN5)(MeCN)$_2$]$^{2+}$ structure is the 119.4° dihedral angle between the acetyl and pyrene groups due to the steric hindrance produced by the alpha-CH groups of each moiety. This avoids potential π−π stacking interactions with the graphitic surface but is responsible for its anchoring via the CH-π interaction as will be discussed below.

![Cyclic voltammetry](image)

**Figure 2. Cyclic voltammetry.** Cyclic voltammograms of 1.0 mM Co-N5 (black lines) and Co-PYN5 (red lines) in dry MeCN containing 0.1 M TBAPF$_6$ as supporting electrolyte, under N$_2$ (dashed lines) and CO$_2$ (solid lines). Experiments performed using a glassy carbon disk as a working electrode, Ag/AgNO$_3$ (0.01 M AgNO$_3$ in MeCN) as reference electrode and a Pt wire as auxiliary electrode at a scan rate of 100 mV/s. The background current under CO$_2$ is shown for comparison (cyan).

The electrochemical properties of Co-PYN5 and Co-N5 were investigated based on cyclic voltammetry (CV) experiments in the presence and absence of CO$_2$ using MeCN as solvent and the results are shown in **Figure 2.** All potentials reported here are measured using ferrocene as an internal standard and transformed to normal hydrogen electrode (NHE) by adding +0.63 V.$^{14,44}$ On the cathodic side, in the absence of CO$_2$ each of the complexes presents a one-electron reduction event in the range of -0.80 to -0.84 V that is associated with the Co(II)L/Co(I)L redox couple, with
an anodic peak at roughly -0.75-0.85 V. Then, in the -1.20 - -1.81 V range Co-N5 presents two redox processes that are associated with two consecutive ligand reductions. The first one at \( E_{p,a} = -1.37 \) V (Co(I)L·/Co(I)L) and the second one at \( E_{p,a} = -1.78 \) V (Co(I)L·−2/(Co(I)L·−)). On the other hand, the Co-PYN5 shows three ligand based redox processes, two of them at the same potentials as Co-N5 and an additional wave at \( E_{p,a} = -1.48 \) V that can be tentatively assigned to the reduction of the pyrene moiety. In the presence of \( \text{CO}_2 \), the first Co(II)/Co(I) cathodic wave for either Co-N5 or and Co-PYN5 remains mainly unaltered and a new catalytic wave appears at \( E_{\text{onset}} = -1.15 \) V, close to the Co(I)L/Co(I)L·− couple, and thus manifesting that the Co(I)L·− species is sufficiently nucleophilic to interact with \( \text{CO}_2 \) and provokes the catalytic reduction of \( \text{CO}_2 \). Based on the above results, little difference is revealed for their catalytic activities.

Further for the case of Co-PYN5, a second catalytic wave appears at \( E_{\text{onset}} = -1.43 \) V that coincides with the pyrene-based reduction mentioned above thanks to a larger degree of \( \pi \)-delocalization. This is interesting because the triply reduced complex in the Co-PYN5 case produces a much more nucleophilic species than the doubly reduced one that will be accessible to the Conduction Band (CB) of the g-C₃N₄ absorber.

The CV experiments of Co-PYN5 and Co-N5 were also registered in the presence 5% TFE under \( \text{CO}_2 \) in MeCN as solvent and are displayed in Figures S1 and S2. Interestingly, as can be observed all potentials cathodically shift by about 200 mV and the onset of catalysis now occurs at approx. -1.0 V. Electrocatalytic experiments were carried out by means of bulk electrolysis for both Co-PYN5 and Co-N5 in MeCN with 5% TFE as a proton source at an applied potential of -1.30 V, giving mainly CO and \( \text{H}_2 \) as products, in ratio of 3.8 and 2.5, respectively (Table S1).

As a visible light absorbing material, we used g-C₃N₄ obtained from the polymerization of urea as described in the literature. To anchor the catalyst into the light absorbing material we prepared a 5 mM Co catalyst solution in 5 mL of MeCN and added 4 mg of g-C₃N₄ powder. Then the mixture was centrifuged and the obtained solid was washed with MeCN and dried at vacuum (see experimental details in the SI).

This generated the hybrid material Co-PYN5@g-C₃N₄, where the catalyst is attached to the surface of g-C₃N₄. Following the same methodology but using Co-N5 without the pyrene functionality did not generate any anchored catalyst at the surface of g-C₃N₄ and thus manifests that the pyrene group is responsible for anchoring at the absorber surface. The absence of Co-N5 at the surface of g-C₃N₄

was evidenced by both UV-vis and 2D grazing incidence wide angle X-ray scattering (GIWAXS) analysis that are reported in the SI as Figures S3 and S4, respectively. To quantify the amount of Co-PYN5 at the surface we carried out inductively coupled plasma (ICP) analysis that gave a value of 2.14 μmol/g.

The non-planarity of the pyrene and pyridyl rings (119.4°) mentioned previously excludes the possibility of conventional π-π interactions between the pyrene group and the nearly planar structure of g-C₃N₄. This leaves CH-π interactions as the only possible bond besides potential van der Waals interactions. This was further confirmed by DFT calculations where we used a continuous VASP model to simulate the g-C₃N₄ surface and using [Co(PYN5)Cl]Cl as a model complex. The results obtained can be graphically observed in Figure 3 where the pyrene group is positioned perpendicular to the g-C₃N₄ surface with two CH groups pointing close to the center of the C₃N₃ hexagonal ring and thus maximizing the interactions. The distances between the CH group and the plane defined by the C₃N₃ ring are 2.13 Å and 2.69 Å, respectively. The calculated adsorption energy is of 11.2 kcal/mol that corresponds to an average of 5.6 kcal/mol per CH-π interaction that is in agreement with those previously reported data.38,40,45,46 An electronic density map of the interaction between the g-C₃N₄ surface and the pyrene group of the Co-PYN5 catalyst is provided in the SI (Figure S5).

Figure 3. DFT calculation. Drawn structure for the Co-PYN5@g-C₃N₄ molecular hybrid material based on DFT calculations. The CH-π interaction and distances between Co-PYN5 and g-C₃N₄, are shown with orange dashed lines while the electron-hole flow during the light induced CO₂ reduction catalysis is indicated with green and black arrows respectively.
Figure 4. Photocurrent measurements. Transient (light on/off) photocurrent responses of $g\text{-}C_3\text{N}_4$ (black), Co-PYN5@$g\text{-}C_3\text{N}_4$ (red) hybrid ink dropped onto an FTO electrode (no bias, 0.5 M NaClO$_4$ solution).

The new hybrid material was further characterized by powder X-ray diffraction (PXRD; Figure S6), diffuse reflectance spectroscopy (DRS; Figure S7) and X-ray photoelectron spectroscopy (XPS; Figure S8) and these results are displayed in the SI. The light absorbing properties of the hybrid material were also characterized based on fluorescence and time-resolved photoluminescence (TRPL) spectroscopy on solid samples (Figures S9 and S10). Further photocurrent responses were also measured on FTO electrodes (Figure 4).

The fluorescence spectra of $g\text{-}C_3\text{N}_4$ show typical emission band at 433 nm. In the presence of either TEOA or Co-PYN5 the emission is partially quenched. Interestingly, when a combination of TEOA and Co-PYN5 is added, the emission is quenched to a larger extend consistent with the electron donating capacity of the TEOA to react with the hole generated upon illumination of the $g\text{-}C_3\text{N}_4$ material and the corresponding reduction of Co(II) to Co(I) by the excited electrons on the CB. A related phenomenon is observed by TRPL with a lifetime of 7.55 ns for $g\text{-}C_3\text{N}_4$ that agrees with previous examples reported in the literature. In the presence of Co-PYN5 and TEOA, there is a significant lifetime reduction that is even more pronounced when both TEOA and Co-PYN5 are present at the same time till 5.40 ns (See detailed information in the SI). Interestingly, bias-free transient (light on/off) photocurrent responses of 0.1 $\mu$A/cm$^2$ for $g\text{-}C_3\text{N}_4$@FTO in a 0.5 M NaClO$_4$ aqueous solution are observed (Figure 4). In the presence of the Co catalyst under the same
conditions the photocurrent response obtained for Co-PYN5@g-C₃N₄@FTO increases 15 times up to 1.5 μA/cm² with practically no attenuation after 8 consecutive illumination cycles.

Figure 5. Photocatalytic CO₂ reduction. (a) Time profiles of photocatalytic CO (star) and H₂ (pentagon) formation from a MeCN/TEOA (v:v = 4:1) solution containing 4.0 mg g-C₃N₄, 5 v% TFE and 50 μM Co-PYN5 (red) or Co-N5 (blue). (b) Time profiles of photocatalytic CO (star) and H₂ (pentagon) formation from a CH₂Cl₂/TEOA (v:v = 4:1) solution containing 4.0 mg Co-PYN5@g-C₃N₄ and 5 v% TFE.

Photocatalytic experiments for the reduction of CO₂ were carried out using the hybrid material Co-PYN5@g-C₃N₄ in a home-made quartz vessel with triethanolamine as a sacrificial electron donor, TFE as proton source and a mercury lamp (λ ≥ 400 nm) as the light source under 1 atm pressure of CO₂. Initially the experiments were carried out by adding g-C₃N₄ (1 g/L) into a MeCN/TEOA (v:v = 4:1) solution containing the Co catalyst. CO was the main product observed. Using labelled ¹³CO₂ allows to confirm that the generated CO comes exclusively from CO₂ (Figure S11).

A typical time profile of [Co-PYN5+g-C₃N₄] system for photocatalytic CO₂ reduction is displayed in Figure 5. Using a [Co-PYN5] of 50 μM and after 8 h of irradiation, 15.4 μmol of CO was detected as the dominant gaseous product, consistent with a 94% CO selectivity and a turnover number (TON) of 77 (Table 1, entry 2). This is in sharp contrast with the electrocatalytic conditions described earlier in homogeneous phase where the CO selectivity is significantly lower. For the Co-N5 catalyst, in the absence of the pyrene group, the species absorbed or in close contact with the surface drastically decreases, giving a TON of 37, which is 2 times lower as compared to the Co-PYN5 in the same conditions (Table 1, entry 5). This comparison clearly manifests that the CH-π interaction
significantly promotes the photocatalytic performance. The increased reactivity of the Co-PYN5 versus Co-N5 can also be observed under the same conditions as previously described but in the absence of TFE, see entries 1 and 4 in Table 1, where the reactivity of the pyrene containing complex is 5 times higher toward the formation of CO.

Given the high solubility of the catalysts in MeCN, an equilibrium between catalyst and \( g-C_3N_4 \) material is established in this solvent, as indicated in the equation below,

\[
g-C_3N_4 (s) + \text{Co-PYN5 (dis)} \rightleftharpoons \text{Co-PYN5@g-C}_3\text{N}_4 (s) \tag{1}
\]

Consequently, only the adsorbed catalytic species, Co-PYN5@g-C\(_3\)N\(_4\), will be active and thus the TON reported here represents a lower limit of the catalyst performance.

**Table 1.** Photocatalytic reduction of CO\(_2\) to CO by cobalt complexes and comparison with reported results for CO\(_2\) reduction to CO in MeCN/TEOA with \( g-C_3N_4 \).

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Catalyst]</th>
<th>[Absorber]</th>
<th>Light source</th>
<th>QE (%)</th>
<th>CO (μmol)</th>
<th>( H_2 ) (μmol)</th>
<th>CO (%)</th>
<th>TON (TOF; h(^{-1}))</th>
<th>Time (h)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co-PYN5 (50 μM)</td>
<td>( g-C_3N_4 (1 g/L) )</td>
<td>Hg lamp (&gt; 400 nm, 180 mW/cm(^2))</td>
<td>0.25 (405 nm)</td>
<td>11.1</td>
<td>0.75</td>
<td>94</td>
<td>55.5</td>
<td>8</td>
<td>rw</td>
</tr>
<tr>
<td>2(^{a})</td>
<td>Co-PYN5 (50 μM)</td>
<td>( g-C_3N_4 (1 g/L) )</td>
<td>Hg lamp (&gt; 400 nm, 180 mW/cm(^2))</td>
<td>0.45 (405 nm)</td>
<td>15.4</td>
<td>0.89</td>
<td>94</td>
<td>77</td>
<td>8</td>
<td>rw</td>
</tr>
<tr>
<td>3(^{b})</td>
<td>Co-PYN5@g-C(_3)N(_4) (2.14 μmol/g)</td>
<td>( g-C_3N_4 (1 g/L) )</td>
<td>Hg lamp (&gt; 400 nm, 180 mW/cm(^2))</td>
<td>N.A.</td>
<td>4.56</td>
<td>0.17</td>
<td>96</td>
<td>533 (95)</td>
<td>8</td>
<td>rw</td>
</tr>
<tr>
<td>4</td>
<td>Co-N5 (50 μM)</td>
<td>( g-C_3N_4 (1 g/L) )</td>
<td>Hg lamp (&gt; 400 nm, 180 mW/cm(^2))</td>
<td>N.A.</td>
<td>2.10</td>
<td>1.14</td>
<td>65</td>
<td>11</td>
<td>8</td>
<td>rw</td>
</tr>
<tr>
<td>5(^{a})</td>
<td>Co-N5 (50 μM)</td>
<td>( g-C_3N_4 (1 g/L) )</td>
<td>Hg lamp (&gt; 400 nm, 180 mW/cm(^2))</td>
<td>N.A.</td>
<td>7.25</td>
<td>1.25</td>
<td>85</td>
<td>37</td>
<td>8</td>
<td>rw</td>
</tr>
<tr>
<td>6(^{c})</td>
<td>Co-PYN5 (50 μM)</td>
<td>( g-C_3N_4 (1 g/L) )</td>
<td>Hg lamp (&gt; 400 nm, 180 mW/cm(^2))</td>
<td>N.A.</td>
<td>6.70</td>
<td>1.30</td>
<td>84</td>
<td>33.5</td>
<td>8</td>
<td>rw</td>
</tr>
<tr>
<td>7</td>
<td>No Cat</td>
<td>( g-C_3N_4 (1 g/L) )</td>
<td>Hg lamp (&gt; 400 nm, 180 mW/cm(^2))</td>
<td>N.A.</td>
<td>0.3</td>
<td>0.32</td>
<td>/</td>
<td>/</td>
<td>8</td>
<td>rw</td>
</tr>
<tr>
<td></td>
<td>Fe(qpy) (20 μM)</td>
<td>mpg-C₃N₄ (2 g/L)</td>
<td>Hg lamp (400 W, &gt; 400 nm)</td>
<td>4.2 (&gt; 400 nm)</td>
<td>12.4</td>
<td>0.1</td>
<td>97</td>
<td>155 (50)</td>
<td>17</td>
<td>27</td>
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<tr>
<td>8</td>
<td>CoPor (2.2 mg)</td>
<td>g-C₃N₄ (10 g/L)</td>
<td>Xe lamp (&gt; 420 nm)</td>
<td>N.A.</td>
<td>0.7</td>
<td>0</td>
<td>&gt;100%</td>
<td>5.8 (1)</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>Fe(TCPP) (0.5 mg)</td>
<td>g-C₃N₄ (2 g/L)</td>
<td>Xe lamp (&gt; 420 nm, 220 mW/cm²)</td>
<td>0.03 (&gt; 400 nm)</td>
<td>2.0</td>
<td>0.35</td>
<td>85</td>
<td>90 (1.8)</td>
<td>48</td>
<td>31</td>
</tr>
<tr>
<td>10</td>
<td>Co(qpy) (3 μM)</td>
<td>mpg-C₃N₄ (0.6 g/L)</td>
<td>Xe lamp (&gt; 400 nm, 100 mW/cm²)</td>
<td>N.A.</td>
<td>0.31</td>
<td>0.04</td>
<td>88</td>
<td>37</td>
<td>24</td>
<td>36</td>
</tr>
<tr>
<td>11</td>
<td>Co(PPc)</td>
<td>mpg-C₃N₄ (2 g/L)</td>
<td>Xe lamp (&gt; 400 nm, 100 mW/cm²)</td>
<td>N.A.</td>
<td>0.25 (&gt; 400 nm)</td>
<td>2.28</td>
<td>0.07</td>
<td>97%</td>
<td>254 (6)</td>
<td>96</td>
</tr>
<tr>
<td>12</td>
<td>Co(qpy-Ph COOH) (1.48 mmol/g)</td>
<td>mpg-C₃N₄ (2 g/L)</td>
<td>Xe lamp (&gt; 400 nm, 100 mW/cm²)</td>
<td>N.A.</td>
<td>0.57 (&gt; 400 nm)</td>
<td>7.6</td>
<td>0.27</td>
<td>97%</td>
<td>513 (2.3)</td>
<td>222</td>
</tr>
<tr>
<td>13</td>
<td>Co(qpy-NH₂) (15 μM)</td>
<td>graphene acid (0.067 g/L)</td>
<td>Xe lamp (&gt; 400 nm, 100 mW/cm²)</td>
<td>N.A.</td>
<td>0.057 (&gt; 400 nm)</td>
<td>0.57</td>
<td>0.27</td>
<td>97%</td>
<td>513 (2.3)</td>
<td>222</td>
</tr>
</tbody>
</table>

[a] Addition of 5 v% TFE.

[b] 4 mL CH₂Cl₂/TEOA (4:1), 5 v% TFE.

[c] 0.1 atm CO₂, 0.9 atm Ar.

[d] MeCN/H₂O/TEOA = 3:1:1

[e] 0.05 M BIH, 0.1 M PhOH.

*TCPP = tetra(4-carboxyphenyl)porphyrin; Por = 3,3’-(8,13-diacetyl-3,7,12,17-tetramethylporphyrin-2,18-diyldipropionic acid; PPc = polyphthalocyanine; qpy-Ph-COOH = 4-((2,2’:6’,2”-quaterpyridin]-4-yl)benzoic acid, qpy-NH₂ = 4-((2,2’:6’,2”-quaterpyridin]-4-yl)phenylamine.

Further, in order to decouple the equilibrium indicated in Equation 1, the photocatalytic experiments were carried out using CH₂Cl₂ as the solvent instead of MeCN, where Co-PYN5 is insoluble. In this case we used the hybrid material Co-PYN5@g-C₃N₄ suspended in a CH₂Cl₂ solution in the presence of TEOA under the same conditions. A TON of 533 is reached that is nearly an order of magnitude larger than that in MeCN (Table 1, entry 3) and is among the largest reported
in the literature for related systems with no noble metals. Further, an initial turnover frequency (TOF; measured during the first two hours) of 95 h\(^{-1}\) is obtained that is among the fastest reported in light induced CO\(_2\) reduction systems using non-noble-metal molecular catalysts and g-C\(_3\)N\(_4\). For comparative purposes, the performances of other relevant molecular catalysts using g-C\(_3\)N\(_4\) as a light absorber are presented in entries 8-13, Table 1, where the interactions with the catalysts and the g-C\(_3\)N\(_4\) semiconductors are based on van der Waals interaction (entry 8 and 12), \(\pi-\pi\) stacking (entries 10, 11) and covalent amide bonds (entries 9, 13). Finally, another feature of our system is that it is also active at [CO\(_2\)] as low as 0.1 atm as indicated in the entry 6 of Table 1. This is interesting because in fuel, oil and coal combusion the flue gas [CO\(_2\)] in dry exhaust gas, is within 10-15% by volume.\(^{48}\)

**Conclusion**

Overall, the results presented here prove that the CH-\(\pi\) interaction between molecular Co catalysts and the g-C\(_3\)N\(_4\) surface provides the ideal electronic interaction for a successful electronic communication between the catalyst and the light absorber. **Figure 6** exhibits an energy diagram containing the main reactions involved, whereas **Figure 3** shows a diagram of the electron and hole flow upon illumination. Visible light irradiation of the g-C\(_3\)N\(_4\) surface produce a relatively long-lived charge-separated excited state (in the ranges of ns) where the positive charge generated at the VB is quenched by excess TEOA that acts a sacrificial electron donor. On the other hand, the electrons at the CB are collected by the molecular Co(II) catalyst undergoing two consecutive reduction events that provoke the transformation of CO\(_2\) into CO, in agreement with the electrochemical results described earlier (**Figure 2**).

In conclusion, we present a very efficient molecular hybrid system composed of g-C\(_3\)N\(_4\) semiconductor and a Co-PYN5 catalyst that contains a pyrene functionality and a protonated site ready for potential intramolecular proton transfer and/or hydrogen bonding. The pyrene moiety acts as an anchoring group that adsorbs the Co-PYN5 complex at the surface of the g-C\(_3\)N\(_4\) dye via CH-\(\pi\) interaction. As consequence of this, the Co concentration at the surface of g-C\(_3\)N\(_4\) is much larger for the Co-PYN5 that contains the pyrene group than for Co-N5 that lacks it under similar conditions. In addition, the hybrid system has the right electronic coupling between the pyrene group and the surface thus providing a low energy pathway for interfacial electron transfer (**Figure S1**).
Further the delocalized $\pi$-system of pyrene interacts with the $\pi$-system of the pyridyl group so that it provides a low energy access to the doubly reduced ligand and the right energy to interact with the CB of $g$-$C_3N_4$. This in turn increases the nucleophilicity of the Co complex, making it much more reactive to atmospheric CO$_2$.

Overall, the understanding ligand effects that include the first and second coordination effects and ligand-based electron transfer capabilities allow to design powerful and selective systems for light induced CO$_2$ reduction catalysis with non-noble metals involved.

**Figure 6. Reaction diagram.** Simplified energy and reaction scheme proposed to operate in the visible light induced CO$_2$ reduction to CO by the molecular hybrid material Co-PYN5@$g$-$C_3N_4$, in the presence of TEOA as a sacrificial electron donor.

**EXPERIMENTAL PROCEDURES**

**Resource Availability**

*Lead contact*

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Antoni Llobet (allobet@iciq.cat).

*Materials availability*

This study generates 4-(pyren-1-yl)-2,6-diacetpyridine, Co-PYN5 and Co-PYN5@$g$-$C_3N_4$ as the new reagents which were obtained by the synthetic procedures below.

*Data and code availability*
All data needed to support the conclusions of this manuscript are included in the main text or the supplemental information.

**Synthesis of 4-(pyren-1-y1)-2,6-diacetipyridine.**

The pyrene-appended compound was prepared by using a modified Suzuki coupling method, where 2.5 mmol of 4-bromo-2,6-diacetipyridine, 2.5 mmol of pyrene-1-boronic acid, 7.5 mmol of K$_2$CO$_3$, 0.25 mmol of Pd(PPh$_3$)$_4$, and a magnetic stirrer were mixed in a 100 mL Schlenk flask, followed by degassing and purging with nitrogen. At the same time, 10 mL of distilled water and 40 mL of THF was also bubbled with nitrogen under stirring for 30 min, then added to the above Schlenk flask. The reaction mixture was left for 1 day at 75 °C, during which yellow solids were generated. Afterwards, ice cool distilled water was added and the mixture was extracted with 4 × 25 mL of CH$_2$Cl$_2$. After evaporation of the solvent, the solid was purified by liquid chromatography. Silica was used as stationary phase. A mixture of petroleum ether/CH$_2$Cl$_2$ = 9:1 was used as mobile phase at the initial stage, and turned to pure CH$_2$Cl$_2$ to get the second crop of eluent. Elemental analysis (C$_{25}$NO$_2$H$_{17}$): Calculated value: C, 82.63; H, 4.72; N, 3.85; Measured value: C, 82.19; H, 4.75; N, 3.70. ESI-MS(+): Calculated for 4-(pyren-1-yl)-2,6-diacetipyridine ([M + H]$^+$, C$_{25}$H$_{18}$NO$_2$) m/z = 364.4, found m/z = 364.4. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.54 (s, 2H), 8.29-7.96 (m, 9H), 2.93 (s, 6H).

**Synthesis of Co-PYN5.**

A sample of 363 mg (1 mmol) of 4-(pyren-1-yl)-2,6-diacetipyridine and 178 mg (0.5 mmol) of Co(CF$_3$SO$_3$)$_2$ were dissolved in 40 mL of toluene/MeCN (v:v = 1:1) at 100 °C under a nitrogen atmosphere. Then, 73 mg (1 mmol) of triethylenetetramine and 0.5 mL anhydrous acetic acid were drop-wise injected into the system, respectively. After 6 h reaction, the solution was cooled to room temperature, dried in vacuum, re-dissolved by adding 50 mL dry CH$_3$OH and filtrated to remove the unreacted reagents. The filtrate was added with 1 g NaClO$_4$ (excess) to precipitate Co-PYN5 as the brown solids, which was isolated by filtration and rinsing with cold alcohol. The single crystals of Co-PYN5 were obtained by liquid diffusion of ether into the concentrated MeCN solution of Co-PYN5. Yield: 205 mg (56 %). Elemental analysis (CoC$_{31}$H$_{31}$N$_5$O$_8$Cl$_2$): Calculated value: C, 50.90;
H, 4.27; N, 9.57; Measured value: C, 51.02; H, 4.18; N, 9.50. ESI-MS(+): Calculated for [Co(PYN5)]^{2+} ([M/2]^+, C_{15.5}H_{15.5}Co_{1/2}N_{2.5}) m/z = 266.2, found m/z = 266.2.

Preparation of Co-PYN5@g-C_{3}N_{4}.

20.0 mg of g-C_{3}N_{4}, 250 μL of 5 mM Co-PYN5 MeCN solution and 2.0 mL of MeCN were mixed and stirred for 2 h, followed by centrifugation and washing with MeCN twice, dried under vacuum. The Co content of Co-PYN5@g-C_{3}N_{4} is estimated as 2.14 ± 0.02 μmol/g (where μmol/g is μmol of Co-PYN5 per gram of Co-PYN5@g-C_{3}N_{4}) by ICP-MS.

SUPPLEMENTAL INFORMATION

Supplemental Information containing experimental details, supporting figures, and calculation data can be found online.

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AUTHOR CONTRIBUTIONS
J.W.W and A.L conceived the idea, designed the experiments and wrote the manuscript. M.G.S performed characterization and wrote the manuscript. H.H.H operated the DFT calculation. E.S carried out the synchrotron experiments. Y.F.M performed the fluorescent experiments. G.O. participated in the discussion and supervised the experiments.

**DECLARATION OF INTERESTS**

The authors declare no competing interests.

**REFERENCES**


