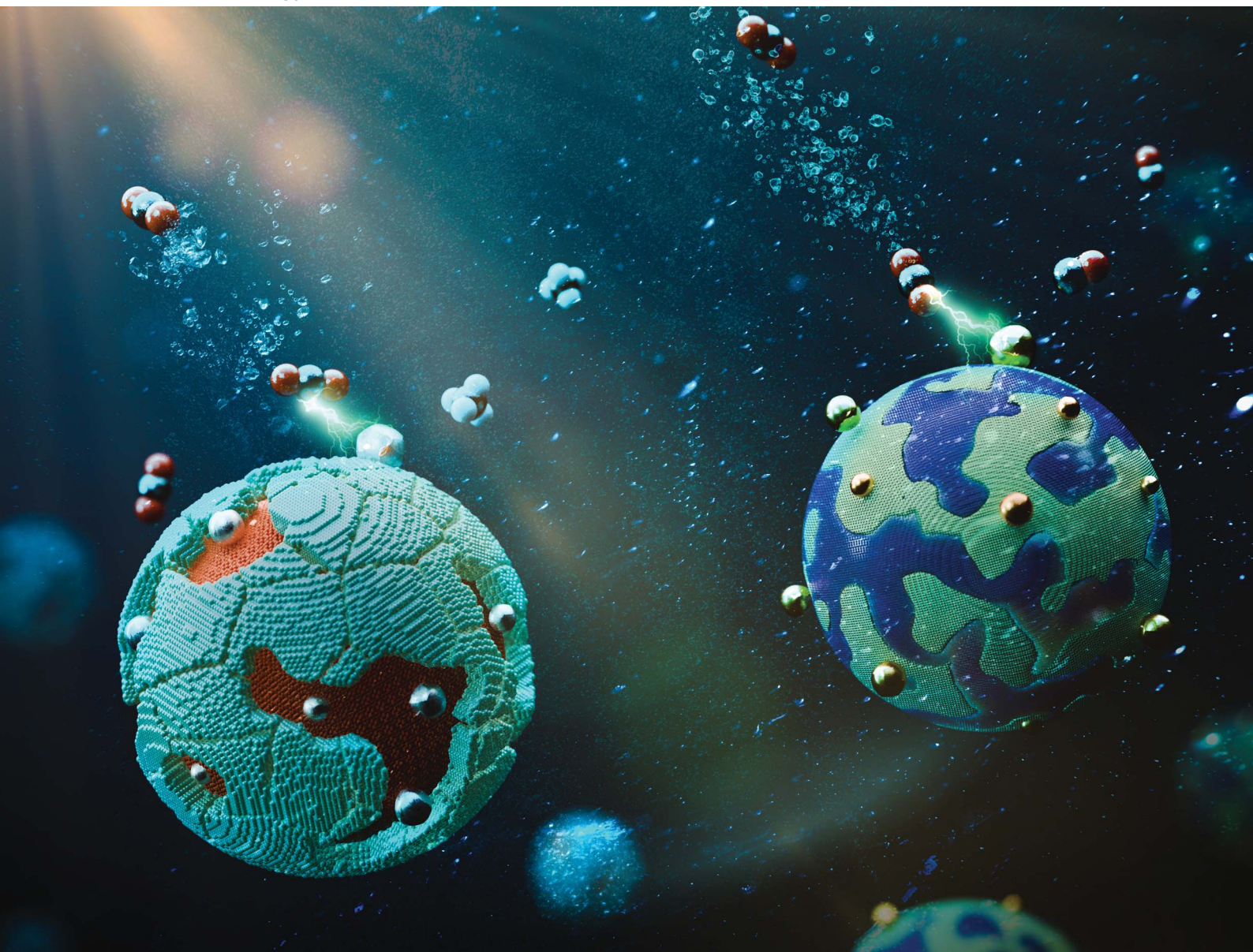


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Organic semiconductor nanoparticles for visible-light-driven CO₂ conversion†

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We present an experimental proof-of-concept study of organic semiconductor nanoparticles (NPs) for visible-light-driven carbon dioxide (CO₂) conversion. Donor:acceptor NPs, consisting of the conjugated polymer donor PM6 and small molecule electron acceptors, namely, PC₇₁BM or Y6, decorated with silver as cocatalyst, produce CH₄ with reaction rates of (3.6 ± 0.8) and (4.2 ± 1.4) μmol g⁻¹ h⁻¹, respectively. NPs consisting of PCE10 as donor polymer and ITIC as small molecule acceptor and decorated with gold as cocatalyst, exhibit CO production rates of (4.7 ± 1.2) μmol g⁻¹ h⁻¹. Importantly, the synergetic effect of efficient cocatalyst deposition and charge carrier generation within the NPs determines their photocatalytic activity.

Photocatalytic water splitting and CO₂ reduction^{1,2} driven by abundant solar energy³ can support the urgently needed transition to a carbon-neutral society, while simultaneously addressing the challenge of intermittency of solar energy by producing energy carriers, namely, solar fuels, compatible with existing energy conversion technologies.^{4,5}

Recently, organic semiconductors such as π-conjugated polymers and small molecules have been designed specifically for photocatalytic CO₂ conversion into value-added products, most commonly CO and CH₄.^{6–10} The ability to tune their energy levels to the targeted redox half-reactions, their strong absorption in the visible to near-infrared (NIR) spectral region, and the solution processibility of these materials make them promising candidates for the task.^{11,12} Yet, short electron-hole pair

(exciton) diffusion lengths in organic semiconductors and their intrinsically high exciton binding energies due to the low dielectric constant of organic materials often limit charge separation and therefore, the photocatalytic activity.^{13,14}

The general approach to overcome the exciton binding energy (about 0.3–0.5 eV) in organic semiconductors is to fabricate so-called type-II heterojunctions from blends of electron donor and electron acceptor semiconductors with offset ionization energies and electron affinities.¹⁵ In fact, the energy offsets provide the required driving force at the donor:acceptor (D:A) heterojunction to separate bound excitons into spatially separated electron and hole polarons.¹⁶ Water-processable organic “bulk heterojunction” nanoparticles (NPs) have already been demonstrated as state-of-the-art particulate visible-light-driven photocatalysts for H₂ evolution from water.^{17–19} However, their potential for photocatalytic CO₂ conversion has not yet been explored.

The work presented here highlights an experimental proof-of-concept study using recently reported¹⁹ and newly designed water-processable organic semiconductor NPs as visible-light active heterogeneous photocatalysts in visible-light-driven CO₂ conversion. We demonstrate that PM6:PC₇₁BM and PM6:Y6 NPs functionalised with Ag as cocatalyst facilitate CO₂ conversion to CH₄ with generation rates of (3.6 ± 0.8) and (4.2 ± 1.4) μmol g⁻¹ h⁻¹, respectively. Additionally, PCE10:ITIC NPs functionalised with Au as cocatalyst generate CO with a reaction rate of (4.7 ± 1.2) μmol g⁻¹ h⁻¹. Ag and Au are used as cocatalysts since they are known to poorly stabilise H* reaction intermediates and therefore, limit the competing H₂ evolution process, while facilitating the CO₂ reduction reaction.^{20,21} Furthermore, we demonstrate that the photocatalytic activity of the NPs and the final reaction products strongly depend on the chosen metal cocatalyst and its particle size and distribution, as well as on the efficiency of free charge carrier generation within the light-harvesting NP.

The NPs were fabricated by a previously reported mini-emulsion process.^{17,22,23} The donor polymer PBDB-T-2F (PM6) was blended with the fullerene acceptor [6,6]-phenyl C71 butyric

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acid methyl ester (PC₇₁BM) or with the small molecule non-fullerene acceptor BTP-4F (Y6), while the donor polymer PTB7-Th (PCE10) was combined with the non-fullerene acceptor, ITIC. The D:A weight ratio was 1:1 in all NP preparation protocols. Sodium 2-(3-thienyl)ethoxybutyl-sulfonate (TEBS) was used as a stabilising surfactant.^{24,25} The average hydrodynamic diameter (Z_{avg}) of all NP batches was 80–100 nm as determined by dynamic light scattering (DLS) experiments (Fig. S1 and Table S1, ESI†).

Visible light makes up more than 40% of solar energy,²⁶ but often remains largely unused in photocatalytic CO₂ conversion due to the use of wide-bandgap (typically metal oxides or nitrides) absorbers. The key advantage of the chosen organic semiconductors is their strong visible light absorption (Fig. S2, ESI†). Additionally, the D:A pairs were chosen to ensure a sufficiently large energetic offset in the blends (Fig. 1), which drives exciton dissociation at the heterojunction and consequently, facilitates efficient generation of free charge carriers.¹⁶ At the same time, the electron affinity of the acceptors compared to the required half-cell electrochemical potentials of CO₂ reduction half-reactions is predicted to provide sufficient driving force for the CO₂ conversion to CO and CH₄.²⁷ Importantly, energy levels of organic semiconductors remain virtually constant regardless of the solution's pH.^{28,29} However, the redox half-reaction potentials typically exhibit the Nernstian shift. Therefore, the driving force for CO₂ reduction increases with the solution's acidity (lower pH); pH = 3.6 ± 0.1 in the suspensions used here.

Ag or Au was photodeposited (targeted fraction: 10 wt%) as a cocatalyst onto the surface of the organic NPs. Ascorbic acid (AA, 0.1 M aqueous solution) was used as a sacrificial electron

donor to facilitate regeneration of the oxidized donor and to inhibit self-oxidation.³⁰

PM6:PC₇₁BM/Ag and PM6:Y6/Ag NPs demonstrated CH₄ production rates of (3.6 ± 0.8) and (4.2 ± 1.4) μmol g⁻¹ h⁻¹, respectively (Fig. 2a and Table S2, ESI†). Both photocatalysts also generated traces of carbon monoxide (CO). PCE10:ITIC/Au produced primarily CO with a rate of (4.7 ± 1.2) μmol g⁻¹ h⁻¹ and in addition traces of CH₄ (Fig. 2b and Table S2, ESI†). Importantly, the reaction rates are comparable and even exceed the rates of prototypical photocatalysts such as titanium dioxide (TiO₂ (P25)) and graphitic carbon nitride (g-C₃N₄) functionalised with Ag and Au cocatalysts, which were measured under identical conditions in our home-built CO₂ reduction setup (Fig. 2 and S3, ESI†).

No reproducible photocatalytic activity was observed for PCE10:ITIC/Ag, PM6:PC₇₁BM/Au, and PM6:Y6/Au photocatalysts. We attribute this to inefficient cocatalyst photodeposition, as discussed further below. Furthermore, no CO₂ reduction products were detected in the reactions where NPs without cocatalysts were used (Fig. S4, ESI†). We attribute this to inefficient charge extraction from organic NPs and consequently, insufficient charge accumulation for these multi-electron reactions, as well as to a weak adsorption of CO₂ molecules at the organic NP's surface, and the absence of suitable reaction centres that could facilitate the multi-electron CO₂ reduction reaction.

Occasionally, we observed that functional NP batches exhibited poor photocatalytic activity towards CO₂ conversion. Therefore, besides the reaction rates, we also determined the yield of fully-functional NP batches. In other words, the yield of

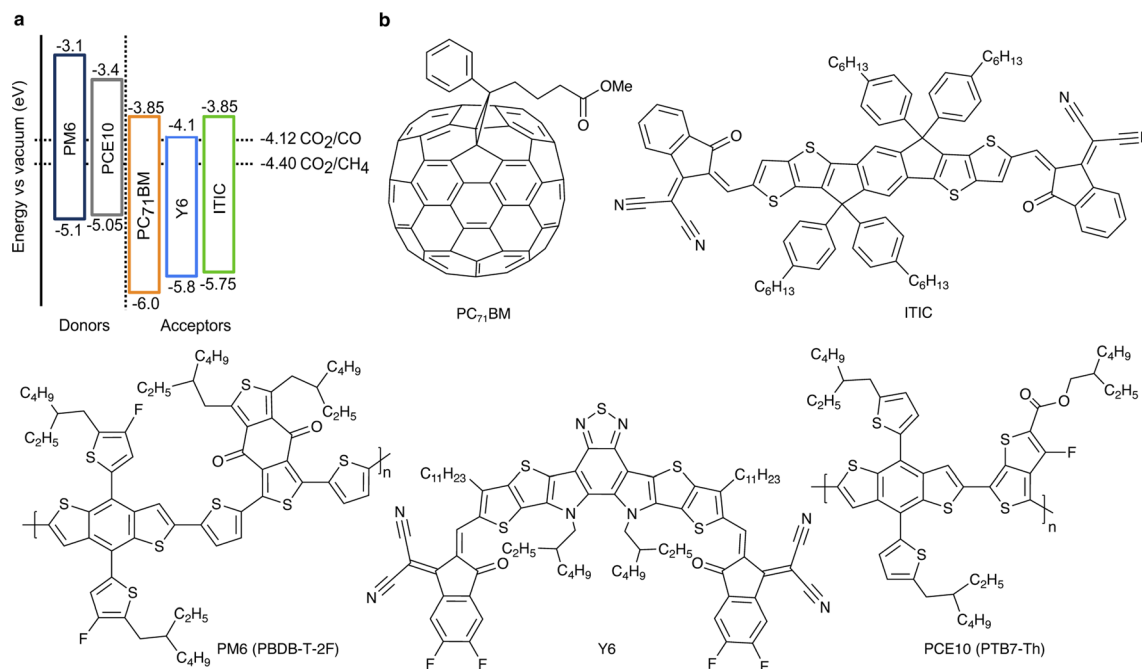


Fig. 1 (a) The organic semiconductors' energy levels compared to the reduction half-reaction potentials of CO₂ conversion into CO and CH₄ at pH = 3.6.²⁷ Ionization energies were determined by ultraviolet photoelectron spectroscopy (UPS) and electron affinities by inverse photoemission spectroscopy (IPES).¹⁶ All energy levels and electrochemical potentials are expressed on the absolute electrochemical scale (0 V vs. SHE = -4.44 V vs. vacuum). (b) Chemical structures of the selected organic semiconductors.



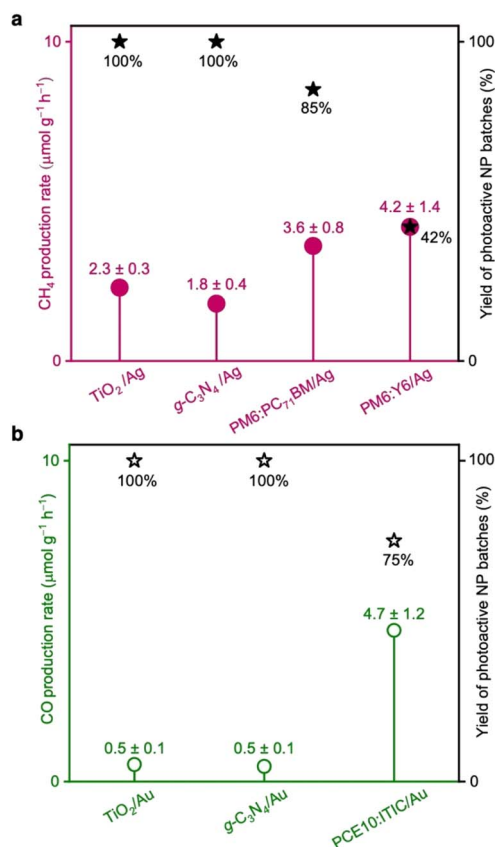


Fig. 2 (a) CH₄ production rates in CO₂ reduction reactions with PM6:PC₇₁BM/Ag and PM6:Y6/Ag NPs. (b) CO production rate in CO₂ reduction reactions with PCE10:ITIC/Au NPs. The results are compared to the rates obtained under identical conditions with the benchmark photocatalysts TiO₂ (P25) and g-C₃N₄, functionalised with Ag or Au cocatalysts. The yield of photoactive NP batches indicates the reproducibility of the production rates across 8 or 10 reactions.

photoactive NPs corresponds to the fraction of separately prepared NP batches that showed photocatalytic activity above a certain threshold. All NP batches that exhibited CO₂ conversion with generation rates less than half of the maximum rates determined for each photocatalyst were considered non-functional. The NP batches showing reactions with rates above the threshold were all considered photoactive and functional. The NP batches showing reactions with rates above the threshold were all considered photoactive and functional. The yield of active PM6:PC₇₁BM/Ag and PM6:Y6/Ag NP batches that generated CH₄ was determined to 85% and 42%, respectively, while the yield of active PCE10:ITIC/Au NP batches that generated CO was 75% (Fig. 2).

Additionally, the NPs' re-usability was tested in separate 12 hour-long reaction cycles. PM6:Y6/Ag could be reused two times before the material aggregated, yet a decrease in the CH₄ production rate was observed between cycles (Fig. S5a, ESI†). PM6:PC₇₁BM/Ag could only be reused once, while PCE10:ITIC/Au aggregated during washing already after the first batch reaction (Fig. S5b, ESI†).

There is a need to improve the yield (reproducibility) of photoactive NP batches and their re-usability, possibly by further optimization of the NP preparation conditions and of the cocatalyst deposition, both part of ongoing works.

Importantly, a series of control experiments were performed to verify the photocatalytic activity of the organic NPs towards CO₂ reduction and to rule out that the obtained products originated from NP degradation (Fig. S4, ESI†). Firstly, no carbon-based products were observed when the reactions were carried out in the dark. Secondly, no carbon-based products were observed in reactions with NP/cocatalyst in an inert (N₂) atmosphere, indicating that no degradation of organic semiconductors due to self-oxidation/reduction under illumination occurred. Thirdly, the competing process of H₂ evolution was strongly suppressed (Fig. S6, ESI†), demonstrating cocatalyst selectivity towards carbon-based products.

Lastly, ¹³C-isotope labelling was employed to determine the origin of the observed CO and CH₄ products. The products of ¹³CO₂ conversion were analysed by gas chromatography coupled with mass spectrometry (GC/MS). In the photoreactions with PM6:PC₇₁BM/Ag and PM6:Y6/Ag as photocatalysts GC/MS spectra revealed the presence of ions with *m/z* = 17 at the retention time (RT = 1.8 ± 0.3 min) corresponding to ¹³CH₄ (Fig. S7a and b, ESI†). In the case of ¹³CO₂ conversion with PCE10:ITIC/Au as photocatalyst, ions with *m/z* = 29 (RT = 7.5 ± 0.3 min) were detected, corresponding to ¹³CO (Fig. S7c, ESI†). Thus, the ¹³C-isotope labelling experiments together with the control reactions confirmed that the products, here, CO and CH₄, were generated by photocatalytic conversion of CO₂ with the aid of organic semiconductor NPs functionalised with either Au or Ag cocatalysts and did not originate from degradation of the organic materials themselves.

To further investigate the observed photocatalysts' activity in relation to their morphology and particle dimensions, the NPs were imaged by cryogenic transmission electron microscopy (cryo-TEM). As reported earlier, PM6:PC₇₁BM NPs with a D : A ratio of 1 : 1 exhibited a core/shell-type structure (Fig. 3a).^{19,31} Here, PC₇₁BM formed the amorphous core and PM6 the semi-uniform shell, as determined from the 2.2 nm lattice spacing observed in the shell, which corresponds to the typical PM6 lamellar stacking distance (Fig. S8, ESI†).³² In accordance with inductively coupled plasma optical emission spectroscopy (ICP-OES) results (Table S3, ESI†), a higher ratio of Ag particles per organic NP (9.3 ± 0.3 wt%) was observed in cryo-TEM images when compared to Au particles (8.5 ± 0.3 wt%) (Fig. 3b and c). Moreover, Au particles were mostly deposited as large clusters, 15–20 nm in size, whereas Ag particle sizes were below 10 nm and the particles were more evenly distributed across the NP surface (Fig. S9, ESI†).

PM6:Y6 NPs exhibit an intermixed structure with randomly distributed semi-crystalline domains (Fig. 3d, S10a and b, ESI†).¹⁹ The areas of enhanced crystallinity with the lattice spacing of ~2 nm correspond to Y6 diffraction peaks observed in thin films (Fig. S11, ESI†).³² Ag cocatalyst photodeposition on the surface of PM6:Y6 NPs resulted in many very small, 1–3 nm, particles (9.9 ± 0.4 wt%). However, large clusters, up to 30 nm, were also observed occasionally (Fig. 3e, S10c and d, ESI†). In the case of Au deposition, predominantly single large particles, 15–20 nm in size, were obtained on the organic NPs surface (Fig. 3f, S10e and f, ESI†). The total amount of the deposited Au



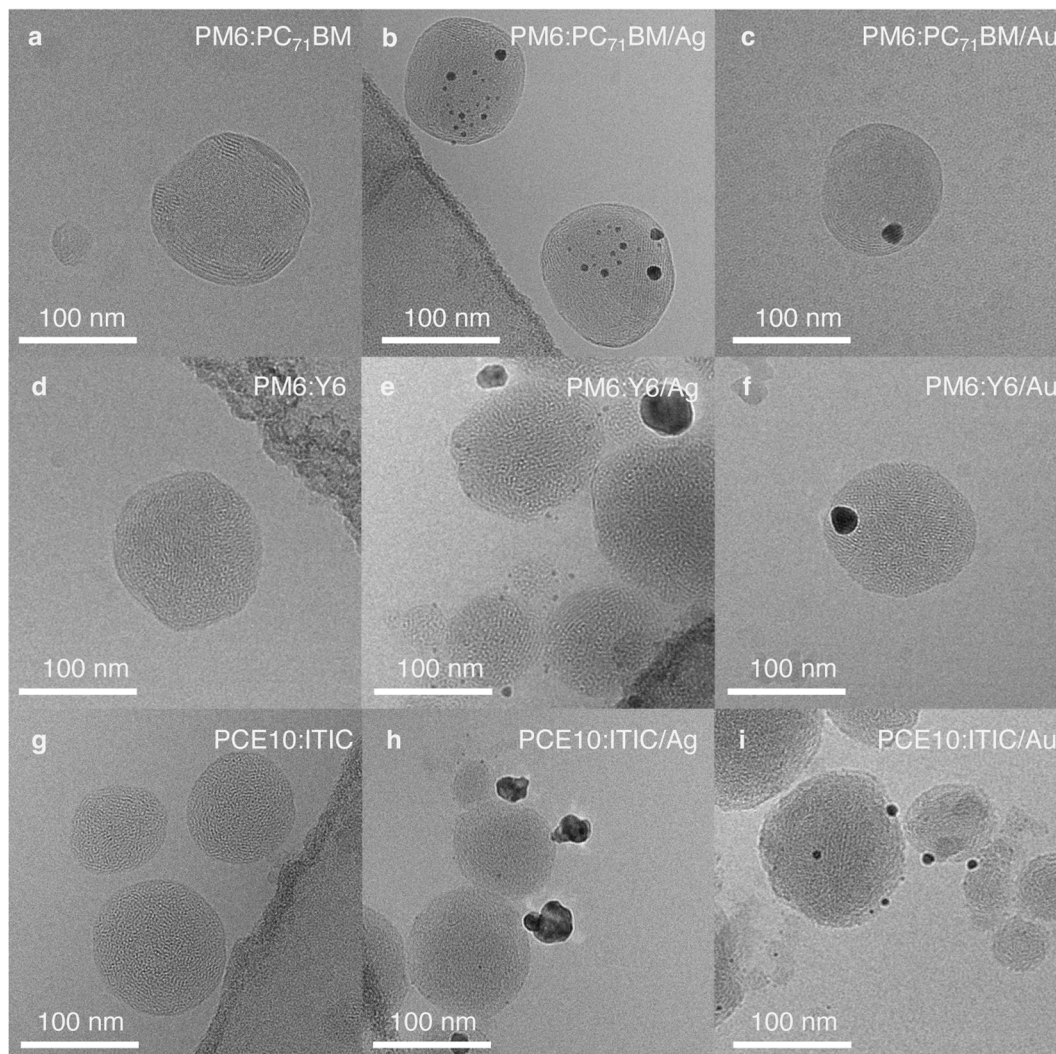


Fig. 3 Bright-field cryo-TEM images of NPs showing their structures and the differences in cocatalyst deposition: (a), (d) and (g), pristine organic NPs of different composition with D : A weight ratio 1 : 1; (b), (e) and (h), corresponding NPs with Ag cocatalyst; (c), (f) and (i), corresponding NPs with Au cocatalyst. Note: the dark contrast in the corners of the images (b), (d), (e), and (g) arises from the carbon TEM grid. Additional images and their analysis are shown in Fig. S8–S16.†

cocatalyst measured by ICP-OES was 8.5 ± 0.3 wt%, which is slightly less than the intended 10 wt%.

PCE10 and ITIC are highly miscible and do not show pronounced phase segregation.³³ Hence, PCE10:ITIC NPs exhibited an intimately mixed structure (Fig. 3g). In some NPs, areas of enhanced crystallinity with 1.9 nm lattice spacing could be observed, which corresponds to the ITIC lamellar stacking distance (Fig. S12, ESI†),^{34,35} while in other NPs, PCE10 lamellar stacking with a lattice spacing of 2.2 nm was found (Fig. S13–S15, ESI†).^{34,36} During photodeposition, Ag formed mostly large clusters (up to 25 nm, 10.0 ± 3.3 wt%) on the PCE10:ITIC surface (Fig. 3h, S14, S16a and b, ESI†). On the other hand, deposition of Au resulted in small particles, typically below 10 nm in size, distributed across the surface of the organic NPs, resulting in a larger cocatalyst surface area available to facilitate CO₂ reduction than in the case of Ag cocatalyst (Fig. 3i, S15, S16c and d, ESI†). Here, the actual Au cocatalyst concentration as determined by ICP-OES was 8.1 ± 0.2 wt%.

Importantly, the concentration, size, and shape of the cocatalyst affect the reactivity of its active sites and can even alter selectivity towards particular reaction products.^{37,38} The surface energy of Au is larger than that of Ag, which makes Au nanoparticles more prone to sintering induced by irradiation with light.^{39,40} Moreover, it has been demonstrated for electrocatalysts that optimal binding and stabilisation of reaction intermediates is possible on the surface of metal nanoparticles less than 10 nm in size.^{41,42} These findings should also apply to cocatalysts in photoreactions. Thus, the negligible photocatalytic activity of PM6:PC₇₁BM/Au, PM6:Y6/Au and PCE10:ITIC/Ag could be attributed to unfavourable cocatalyst deposition, such as single large metal clusters (above 10 nm in size) on the organic NPs' surface. In fact, PM6:PC₇₁BM/Ag, PM6:Y6/Ag and PCE10:ITIC/Au, which exhibit smaller and more evenly distributed cocatalyst particles across the surface of the organic NPs, successfully perform CO₂ conversion to CH₄ and CO, respectively. Nevertheless, the relatively large variance



The TAS spectra of PCE10:ITIC/Au NPs exhibit a broad PCE10 and ITIC GSB at 600–750 nm, together with photoinduced absorption of ITIC anions (ITIC⁻) at 810 nm and PCE10 cations

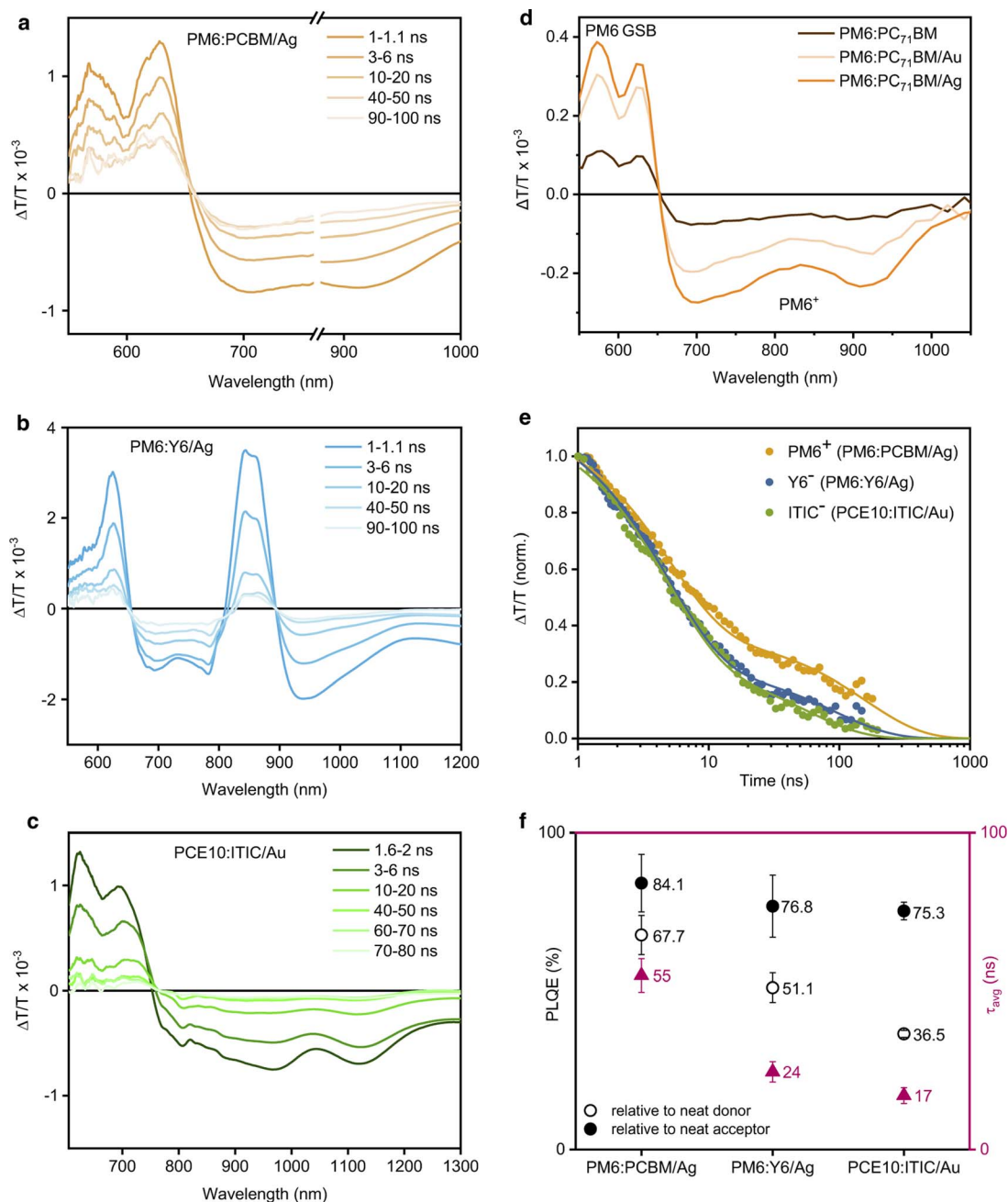


Fig. 4 Photophysical characterisation of D:A/cocatalyst NP dispersions. (a)–(c) Transient absorption spectra at different time delays following 532 nm photoexcitation of PM6:PC₇₁BM/Ag (fluence 11.7 $\mu\text{J cm}^{-2}$), PM6:Y6/Ag (fluence 31 $\mu\text{J cm}^{-2}$), and PCE10:ITIC/Au (fluence 11.7 $\mu\text{J cm}^{-2}$) respectively. (d) Comparison of the PIA spectra of PM6:PC₇₁BM NPs suspensions with and without metal cocatalysts (absorbance 0.28, 1 mm pathlength) following 515 nm photoexcitation (1.93 W cm^{-2}). (e) Comparison of the transient absorption decay dynamics of the corresponding photocatalysts, probed at 757–758 nm for PM6⁺ in PM6:PC₇₁BM/Ag, at 920–950 nm for Y6⁻ in PM6:Y6/Ag, and at 770–890 nm for ITIC⁻ in PCE10:ITIC/Au.^{46–48} (f) Comparison of the charge carrier lifetimes (τ_{avg}) and PL quenching efficiencies (PLQE) of the corresponding photocatalysts.

(PCE10⁺) at 1120 nm, as well as the overlapping photoinduced absorption from ITIC⁻ electron and PCE10⁺ hole polarons at 870–1030 nm (Fig. 4c).⁴⁸ The corresponding ITIC⁻ (anion) kinetics revealed the presence of free charge carriers with an average lifetime of (17.0 ± 2.5) ns (Fig. S24, ESI[†]). In this case, the presence of a metal cocatalyst did not have any effect on the charge carrier kinetics observed in TAS.

However, the PCE10⁺ (cation) PIA signal amplitude of PCE10:ITIC/Au was larger than that of PCE10:ITIC and PCE10:ITIC/Ag, indicative of enhanced hole transfer from the ITIC acceptor to the PCE10 donor in the presence of Au (Fig. S25, ESI[†]). Thus, it appears that the favourable Au deposition onto the PCE10:ITIC NPs' surface enables efficient CO₂ adsorption, facilitates charge transfer, and hence, determines the photocatalytic activity of PCE10:ITIC/Au.



It has previously been shown that the photocatalytic activity of the NPs is determined by the presence of free charge carriers in the NP bulk rather than by the density of catalytically active sites.⁴⁹ Importantly, Ag and Au cocatalysts have demonstrated the ability to capture and store electrons, which causes the Fermi level to shift.⁵⁰ The smaller the metal particle size, the more the Fermi level shifts toward more negative potentials (*vs.* NHE) and the higher the semiconductor's photocatalytic activity becomes.⁵¹ CO₂ reduction to CH₄ requires 8 electrons and 8 protons, while CO₂ reduction to CO is a less demanding process with only 2 electrons and 2 protons.²⁷ Therefore, in the photocatalytic reactions with PM6:PC₇₁BM/Ag and PM6:Y6/Ag NPs, we attribute the CH₄ production to the more efficient generation of long-lived free charge carriers along with efficient electron transfer and charge accumulation at the surface reaction sites by the Ag cocatalyst. However, even though Au has been shown to release accumulated electrons faster than Ag,⁵² the modest exciton quenching efficiency in PCE10:ITIC NPs leads to moderate charge carrier generation and thus, limits the photocatalytic activity of this system (Fig. 4d and e). However, it appears that the amount of electrons accumulated in the cocatalyst of PCE10:ITIC/Au NPs is sufficient to drive the 2-electron CO₂ reduction reaction to CO, consequently, resulting in CO as a major product.

Conclusion

We have successfully demonstrated that organic semiconductor heterojunction NPs photocatalytically reduce CO₂ into CO and CH₄ in suspension under visible light irradiation. PM6:PC₇₁BM/Ag and PM6:Y6/Ag NPs achieved CH₄ generation rates of (3.6 ± 0.8) and (4.2 ± 1.4) μmol g⁻¹ h⁻¹, respectively. The PCE10:ITIC/Au photocatalyst exhibited a CO generation rate of (4.7 ± 1.2) μmol g⁻¹ h⁻¹. Efficient cocatalyst deposition is critical to obtain high photocatalytic activity. Smaller, uniformly distributed cocatalyst nanoparticles provided a larger surface area for CO₂ adsorption and possibly stabilised the reaction intermediates. Photophysical characterisation using TRPL, TA, and PIA spectroscopies revealed that the photogenerated excitons are quenched efficiently due to the D:A heterojunction in these NPs, generating charge carriers with lifetimes on the microsecond timescale, which is sufficiently long to drive photoredox reactions. The charges, in turn, are transferred to the metal cocatalysts and to the surface reaction sites where they drive CO₂ reduction reactions. The yield of products obtained in CO₂ conversion reactions seems to depend on the number of free charge carriers photogenerated in the organic NPs and accumulated at the surface reaction sites of the metal cocatalysts. Thus, further enhancing the efficiency with which charges are transferred to the metal cocatalysts seems crucial for the advancement of photocatalytic organic D:A NPs for CO₂ conversion.

Author contributions

M. F., J. K. conceived the idea. M. F., N. A., L. Z., C. S. P. C. performed the experiments. C. E. P. contributed to data analysis. I. M., M. H., F. L. supervised the project. M. F. wrote the first draft of the paper and all authors contributed to the final version.

Conflicts of interest

There are no conflicts to declare.

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