Electronic Supplementary Information

Organic semiconductor nanoparticles for visible-light-driven CO₂ conversion

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Materials and Methods

Materials. PM6, PCE10, PC₇₁BM, Y6, and ITIC were purchased from Organtec Ltd-BETTERCHEM. Sodium 2-(3-thienyl)ethyloxybutylsulfonate (TEBS) was purchased from Solaris Chem. TiO₂ (P25, nanopowder, particle size < 100 nm) was purchased from Sigma-Aldrich. g-C₃N₄ was generously provided by Dr V. Kale, Functional Materials, Design, Discovery & Development group (FMD³), KAUST. All materials were used without further purification.

Nanoparticle fabrication. Individual stock solutions (0.5 mg ml⁻¹) of PM6, PCE10, PC₇₁BM, Y6, and ITIC were prepared in chloroform. The solutions were stirred and heated overnight (40 °C, 1000 rpm) in the dark to ensure complete dissolution. Nanoparticle precursor solutions were prepared from the stock solutions by mixing the polymer donors with the chosen acceptors in 1:1 weight ratio. Nanoparticle precursor solution (5 ml) was then added to a 0.5 wt.% aqueous solution of TEBS surfactant (10 ml, filtered through 0.45- μ m PVDF) and stirred vigorously (1500 rpm) for 15 min at 40 °C to form a pre-emulsion, which was then sonicated for 5 min with an ultrasonic processor (Sonics VibraCell VCX130PB) to form a mini-emulsion. The mini-emulsion was heated to 80 °C under a stream of N₂ while stirring at 150 rpm for approx. 2 h to remove the chloroform, leaving a surfactant-stabilized nanoparticle dispersion in water. If necessary, the dispersion was filtered (0.45- μ m PVDF) to remove any large aggregates or debris from the processor tip.

NP fabrication is a meticulous process and should be done with extreme care to ensure as high reproducibility as possible. We observed that several parameters influence NP preparation and can result in NPs of unfavourable sizes and morphology: 1) phase segregation between the aqueous surfactant and D:A solution in chloroform during pre-emulsion

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formation, 2) excessive foam formation during sonication, 3) sonication power distribution within the solution volume dependant on the position of the sonicator tip, 4) vortex formation due to vigorous stirring during chloroform evaporation, causing the collision of nanodroplets.

Cocatalyst photodeposition. To achieve approx. 10 wt.% of metal deposition aqueous stock solution of $AgNO_3$ or $HAuCl_4$ (metal concentration 1 mg ml⁻¹, 250 µl) was added to the nanoparticles dispersion in water. The mixture was stirred at 300 rpm and illuminated with a solar simulator (Asahi Hal-320, AM1.5G, 1 sun) for 30 min. Then the dispersion was filtered, rinsed with DI water twice to remove unreacted metal salt, and concentrated via centrifugal dialysis (regenerated cellulose filter 50 000 NMWL). The supernatant was collected for the quantification of the remaining metal ions by inductively coupled plasma optical emission spectrometry (ICP-OES), while the filtrate was used for the reaction.

Dynamic light scattering

The size distribution of each nanoparticle batch was measured by dynamic light scattering (Malvern Zetasizer ZS). Fig. S1 and Table S1 show that all NP batches had unimodal size distributions and that the average hydrodynamic diameter (Z_{avg}) between batches remained relatively constant at 80 – 100 nm. Overall, all NP batches were of a similar size.

Since the charge carrier diffusion lengths in organic semiconductors are about few tens of nm at best, most charge carriers may not reach the cocatalysts and remain in the bulk of the large NPs, thereby limiting the overall photocatalytic activity. Therefore, NPs with sizes \leq 100 nm are preferred, which also exhibit an increased surface/volume ratio, and thus are expected to show more efficient charge generation and charge transfer to the cocatalyst, and further to the reactants.



Fig. S1. Dynamic light scattering (DLS) size distributions by intensity of NPs formed with donor:acceptor (1:1 weight ratio) blends, and the NPs with cocatalysts.

NP composition/ cocatalyst	Average hydrodynamic diameter (nm)	Dispersity
PM6:PC ₇₁ BM	81	0.12
PM6:PC ₇₁ BM/Ag	80	0.12
PM6:PC ₇₁ BM/Au	90	0.13
PM6:Y6	84	0.15
PM6:Y6/Ag	86	0.16
PM6:Y6/Au	89	0.19
PCE10:ITIC	94	0.17
PCE10:ITIC/Ag	91	0.16
PCE10:ITIC/Au	96	0.17

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Steady-state UV-Vis absorption



Fig. S2. Normalised absorption spectra of organic semiconductor nanoparticle dispersions in water.

CO₂ conversion reactions and control experiments

Aqueous nanoparticle dispersion (1.4 ml, 0.7 mg ml⁻¹) with ascorbic acid (AA, 100 μ L, 0.1 M aqueous solution) were loaded into a stainless steel batch reactor (pH = 3.6 ± 0.1) connected in-line to a gas analyser Thermo 1310 equipped with a molecular sieve 5A column and thermal conductivity detector (TCD) for permanent gases and Rt-Alumina BOND/Na₂SO₄ column with flame ionisation detector (FID) for hydrocarbons. A calibration gas mixture (Agilent Technologies UN1954, RGA checkout sample with Argon) was used to set the instrument method and plot the calibration curves for each product. The reactor was evacuated and purged with N₂ at least 6 times to remove air before the reaction. Then the reactor was filled with CO₂ gas (Alphagaz, HP 99.995 %), the pressure was set to 2.5 bar and the dispersion was stirred and illuminated overnight with a solar simulator (Asahi Hal-320) fitted with a UV-IR mirror module and an AM1.5G filter. The pressure drop to 2.3 – 2.4 bar over the first 1 – 3h can be observed as a sign of CO_2 saturation in water. The illumination area was 7.1 ± 0.1 cm². The light intensity at the sample surface was adjusted to 100 mW cm⁻² (1 Sun) before each experiment using a calibrated reference solar cell (Newport 91150V). At the end of the reaction, the gas mixture was injected into the GC sample loop via the pressure drop between the reaction chamber and the injection line, the latter was evacuated to 0.01 bar before the measurement. The experimental setup scheme is shown in Fig. S3.

The identical procedure was used when measuring CO_2 conversion rates with TiO_2 (P25) and $g-C_3N_4$ with Au and Ag cocatalysts (2 wt.%). Except in this case, 50 mg of a photocatalyst was used and the reaction was performed with *i*-propanol or triethanolamine (10 vol. %) as a sacrificial electron donor.

It was noticed that the reduction in the NP photocatalyst concentration to below 0.5 mg ml⁻¹ does not improve the production rates but results in irreproducible reaction yields. Conversely, we found that the NPs were prone to aggregation when their concentration was increased above 1 mg ml⁻¹ at a CO₂ pressure of 2.5 bars, resulting in poor photocatalytic activity.

To calculate the yield of photoactive NP batches, the reaction with PM6:PC₇₁BM/Ag and PCE10:ITIC/Au was repeated under identical conditions 8 times each, and with PM6:Y6/Ag it was repeated 10 times. A fresh photocatalyst batch prepared from fresh stock solutions was used each time.

Photocatalyst	Product		Production rates	
	-	µmol g⁻¹ h⁻¹	µmol h⁻¹	µmol h ⁻¹ cm ⁻²
PM6:PC ₇₁ BM/Ag	CH ₄	3.6 ± 0.8	0.024 ± 0.005	0.003 ± 0.001
PM6:Y6/Ag	CH_4	4.2 ± 1.4	0.044 ± 0.019	0.006 ± 0.003
PCE10:ITIC/Au	СО	4.7 ± 1.2	0.06 ± 0.01	0.009 ± 0.001

Table S2. Rates of CO₂ conversion reactions with different units for comparison.



Fig. S3. Schematic representation of the home-built CO₂ photoreduction setup.



Fig. S4. Chromatograms of products from CO_2 conversion reactions with NP photocatalysts, as well as control experiments without illumination (CO_2 atm.), without a cocatalyst (CO_2 atm.), and in an inert (N_2) atmosphere.

Note: CH_4 produced by PM6:PC₇₁BM/Ag and PM6:Y6/Ag photocatalysts can be detected by both detectors, TCD and FID. CO was reproducibly detected only in the reaction with PCE10:ITIC/Au. No products were reproducibly and quantifiably detected in the reactions without illumination, without a metal cocatalyst, and in an inert (N₂) atmosphere, indicating that CO_2 is required as a reactant.



Fig. S5. Recyclability testing of NP photocatalysts: **a**, production rates in the cycles performed. **b**, photographs demonstrating NPs' aggregation and deposition on the filter after multiple washes using centrifugal dialysis, which is determined to be a major bottleneck in their recyclability.

Note: after 12 h long reaction, the photocatalyst was collected, washed and concentrated via centrifugal dialysis. Then it was reloaded into the reactor with a fresh sacrificial agent. The process was repeated as many times as it was possible to recover most of the photocatalyst from the filter. The decrease in photocatalytic activity between 1st and 2nd cycles for PM6:PC₇₁BM/Ag and between the three cycles for PM6:Y6/Ag can also be attributed to partial aggregation of NPs. That led to the losses of material on the filter, reduced the number of photocatalytically active sites and possibly reduced the efficiency of charge generation.



Fig. S6. a, Chromatogram showing H₂ peak from the calibration gas, and no H₂ product observed in CO₂ conversion reactions performed in the custom-built CO₂ conversion setup connected in-line to GC/TCD with Helium carrier gas. **b,** H₂ generation with the rate of 0.13 μ mol g⁻¹ h⁻¹ is observed in the custom-built H₂ evolution setup when using the PCE10:ITIC/Au photocatalyst, as well as traces of H₂ product generated with PM6:PCBM/Ag and PM6:Y6/Ag. The experiment was performed under identical conditions as the CO₂ conversion, however, in this case, in an inert (Ar) atmosphere. The reactor was connected in-line to GC/TCD with Argon as carrier gas, which provides significantly higher sensitivity for H₂ production than Helium as carrier gas and thus allows the detection of traces (nmol) of generated hydrogen.¹

¹³C-CO₂ isotope labelling. To reveal the carbon source in the photoreaction products ¹³C isotope labelled CO₂ gas (Sigma Aldrich, 99 atom % ¹³C, < 3 atom % ¹⁸O) was used in the photocatalytic reaction following the same procedure described above. The reactor was connected in-line to a Thermo Trace 1300 gas chromatographer mass spectrometer ISQ 7000 (GC/MS) with electron ionisation (EI) equipped with an HP molecular sieve column for ¹³CO identification without N₂ interference, and a TG Bond-Q column for ¹³CH₄. The standard gas mixture of C1 – C3 hydrocarbons, CO, N₂, O₂, CO₂ and Ar (Abdullah Hashim Industrial Gases) was used to set the instrument method and to identify the analytes' retention times. Chromeleon software was used to control the instrument and process the data.



Fig. S7. Mass spectra (single ion monitoring (SIM) mode) indicating the presence of ${}^{13}CH_4$ as product (m/z = 17 (M⁺), RT = 1.8 ± 0.3 min) obtained in CO₂ conversion with **a**, PM6:PC₇₁BM/Ag, and **b**, PM6:Y6/Ag; **c**, ${}^{13}CO$ product (m/z = 29 (M⁺), RT = 7.6 ± 0.3 min) obtained in CO₂ conversion with PCE10:ITIC/Au.

Inductively-coupled plasma optical emission spectroscopy

Table S3. Residual Ag and Au concentrations in the supernatant after their photodeposition measured by inductively-coupled plasma optical emission spectroscopy (ICP-OES), and the corresponding amount (wt.%) of cocatalyst deposited.

NPs	Residual Ag (μg)	Ag deposited (wt.%)	Residual Au (µg)	Au deposited (wt.%)
PM6:PC ₇₁ BM	17.8 ± 0.5	9.3 ± 0.3	39.0 ± 1.4	8.5 ± 0.3
PM6:Y6	2.5 ± 0.1	9.9 ± 0.4	41.7 ± 1.5	8.5 ± 0.3
PCE10:ITIC	1.2 ± 0.4	10.0 ± 3.3	51.2 ± 1.3	8.1 ± 0.2

Cryogenic transmission electron microscopy

Cryo-TEM was carried out with a Thermo Fisher Scientific Titan Krios G2 TEM operated at 300 kV equipped with a Gatan GIF Quantum 968 energy filter and a Gatan K2 direct electron detector, to enable the recording of high-resolution images at low electron dose conditions. Specimen preparation of cryo-TEM samples was carried out by using an automated plunge-freezing tool (Vitrobot Mark-IV). The specimens were prepared on holy carbon copper TEM grids (C-flat MultiH). A 3 μ l portion of the nanoparticle dispersion was placed on the grid followed by 3 seconds of blotting time and plunge-freezing into liquid ethane. Afterwards, all the operations were under liquid nitrogen temperature. The images were recorded under dose-fractionation condition. Images were acquired in EFTEM mode at 130 k× magnification with a total dose of ~50 e/Å². Image acquisition and processing were performed using Gatan Digital Micrograph Suite v.3.2.

PM6:PC71BM-based photocatalyst



Fig. S8. a, Bright field cryo-TEM image of PM6:PC₇₁BM (1:1) NP with core/shell structure before cocatalyst photodeposition. **b**, Inverse FFT of the area in the red rectangle in image a. **c**, Profile of the periodic spacing in the light blue rectangle in image b.



Fig. S9. Bright field cryo-TEM images of PM6:PC₇₁BM (1:1) NPs with **a**, **b**, Ag cocatalyst; **c**, **d**, Au cocatalyst, here some NPs exhibit only very few or none Au particles on their surface, while others exhibit large clusters of Au on their surface.

Note: the PM6 shell was not uniform and areas exposing $PC_{71}BM$ were also present. During cocatalyst photodeposition, the reduction of metal ions occurs at the acceptor-rich areas of the NP surface by electrons, which are localized on the acceptor due to the formation of type II D:A heterojunction. Thus, the photodeposited cocatalyst is likely to be located on the exposed acceptor's surface.

PM6:Y6-based photocatalyst



Fig. S10. Bright field cryo-TEM images of **a**, **b**, PM6:Y6 (1:1) NPs with intermixed structure before cocatalyst deposition, and PM6:Y6 with **c**, **d**, Ag cocatalyst; **e**, **f**, Au cocatalyst, here many NPs appear without any cocatalyst due to large metal clusters concentrated only on some NPs.



Fig. S11. **a**, Bright field cryo-TEM image of PM6:Y6 (1:1) NP with intermixed structure before cocatalyst photodeposition. **b**, Fourier transform of the area in the red rectangle in image a. **c**, Profile of the periodic spacing of the reciprocal lattice in the light blue rectangle in image b.

PCE10:ITIC-based photocatalyst



Fig. S12. **a**, Bright field cryo-TEM image of PCE10:ITIC (1:1) NP with intermixed structure before cocatalyst photodeposition. **b**, Inverse FFT of the area in the red rectangle in image a. **c**, Profile of the periodic spacing in the top left light blue rectangle in image b. **d**, Profile of the periodic spacing in the bottom right light blue rectangle in image b.



Fig. S13. **a**, Bright field cryo-TEM image of PCE10:ITIC (1:1) NP with intermixed structure before cocatalyst photodeposition. **b**, Inverse FFT of the area in the red rectangle in image a. **c**, Profile of the periodic spacing in the light blue rectangle in image b.



Fig. S14. **a**, Bright field cryo-TEM image of PCE10:ITIC/Ag. **b**, Inverse FFT of the area in the red rectangle in image a. **c**, Profile of the periodic spacing in the light blue rectangle in image b.



Fig. S15. **a**, Bright field cryo-TEM image of PCE10:ITIC NPs/Au. **b**, Inverse FFT of the area in the red rectangle in image a. **c**, Profile of the periodic spacing in the light blue rectangle in image b.



Fig. S16. Bright field cryo-TEM images of PCE10:ITIC (1:1) NPs with: **a**, **b**, Ag cocatalyst, and **c**, **d**, Au cocatalyst.

Photophysical characterisation

Time-resolved photoluminescence. The TRPL measurements of the degassed aqueous nanoparticles dispersions (purged with N₂ for 30 min) were performed without flow or stirring as no evidence of time dependence was observed (from 0.2 pJ cm⁻² to 527.3 nJ cm⁻² – but only plotted here at fluences at which no dependence was observed). For these measurements, we used the output of a modelocked Ti:Sa (Chameleon Ultra I from Coherent) fs laser operating at 80 MHz repetition rate, at 450 (SHG pumped at 900 nm), and 532 and 650 nm (OPO-SHG pumped at 800 and 780 nm, respectively), and 780 nm through a Chameleon Compact OPO-VIS, to selectively excite the different donors and acceptors studied as stated along the manuscript. The PL of the samples was collected by an optical telescope (consisting of two plano-convex lenses), focused on the slit of a spectrograph (Princeton Instrument Spectra Pro SP2300) and detected with a Streak Camera (Hamamatsu C10910) system, an appropriate long-pass filter (458, 561, 664-700 nm, and 808 nm, respectively) was used when needed. Measurements on each sample were repeated ~5-7 times to investigate time, fluence and excitation dependence, other spectral regions, different time ranges and account for sample variability. The instrument response function was acquired for each set of measurements with LUDOX and water. The data were acquired in photon counting mode using the Streak Camera software (HPDTA) and exported to Origin 2021 for further analysis. The presented data is not corrected for sensitivity. The TRPL decays were tail fitted, analysed with a sum of exponentials, and the amplitude weighted average lifetime was calculated. The PL quenching efficiency was then calculated according to the reported procedure.²

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Transient absorption spectroscopy. TA pump-probe measurements of the degassed aqueous nanoparticles dispersions (purged with N₂ for 30 min) were carried out with a custom-built setup. A fraction of 0.47 mJ output of a titanium:sapphire amplifier (Coherent LEGEND DUO, 4.7 mJ, 3 kHz, 100 fs) was focused into a c-cut 3-mm-thick sapphire window, thereby generating a white-light supercontinuum from 500 to 1,600 nm. The excitation pulse was provided by an actively Q-switched Nd:YVO₄ laser (InnoLas picolo AOT) frequency-doubled, providing pulses at 532 nm. The pump laser was triggered by an electronic delay generator (Stanford Research Systems DG535) itself triggered by the transistor-transistor logic sync from the Legend DUO, allowing control of the delay between pump and probe with a jitter of roughly 100 ps. Pump and probe beams were both focused on the sample to spot sizes of 1.4 mm and 0.12 mm diameter (from a Gaussian fit at 86.5 % intensity), as measured using a beam profiler (Coherent LaserCam-HR II). The transmitted fraction of the white light was guided to a custom-made prism spectrograph (Entwicklungsbüro Stresing). It was dispersed by a prism onto a 512-pixel CMOS linear image sensor (Hamamatsu G11608-512A). The probe pulse repetition rate was 3 kHz, the excitation pulses were mechanically chopped to 1.5 kHz, and the detector array was read out at 3 kHz. Adjacent diode readings corresponding to the transmission of the sample after excitation and in the absence of an excitation pulse were used to calculate $\Delta T/T$. Measurements were averaged over several thousand shots to obtain a good signal-to-noise ratio. The TA data were analysed using custom-developed MATLAB code.

Photoinduced absorption spectroscopy. Quasi steady-state PIA experiments were performed with white light generated from a 100 W quartz tungsten halogen light source (Newport) used as probe (spot size approx. 0.8 cm^2) and the output of a Cobolt MLD 515 nm laser (18.8 mW) or Cobolt 06-MLD 660 nm laser (28.6 mW) used as pump (spot size 1.5 mm^2). The transmitted probe light was detected after dispersion by a monochromator (LOT Quantum Design MSH 300) by an amplified silicon photodetector (Thorlabs DET10A/M) in the wavelength range 200 – 1100 nm, and by an InGaAs biased detector (Thorlabs DET10D/M) in the wavelength range 800 – 2600 nm. The pump light analog modulation frequency was 346.5 Hz for all measurements. The change in transmission induced by the pump was extracted using the lock-in amplifier (Stanford Research systems, model SR830 DSP). Prior to the PIA measurements, the total transmission was measured to calculate $\Delta T/T$:

$$\frac{\Delta T}{T} = \frac{(PL + PIA)_E - PL_E}{T}, \text{ where E is photon energy}$$

The white light was chopped at 10 Hz by a mechanical chopper. The NPs suspensions of the same composition were prepared with an equal absorbance value at the excitation wavelength and purged with N_2 for 1 hour before the measurements.



Fig. S17. Extinction coefficients for donor and acceptor neat films² indicate that at 532 nm excitation, PM6 (PBDB-T-2F) should be more selectively excited than PC₇₁BM or Y6, and at 780 nm Y6 can be selectively excited.

PM6:PC71BM-based photocatalyst



Fig. S18. Normalized TRPL spectra (averaged from ~0 to 2 ns) of aqueous nanoparticles dispersions: **a**, neat PM6 (black) and neat PCBM (red). **b**, PM6:PCBM. **c**, PM6:PCBM/Ag. **d**, PM6:PCBM/Ag + ascorbic acid (AA). **e**, PM6:PCBM/Au, and **f**, PM6:PCBM/Au + AA, with λ_{exc} = 450 and 532 nm. Note: water Raman signal can be seen at ~834 nm for the lower emission spectra with excitation 532 nm.³

Table S4. Averaged lifetimes and PL quenching efficiencies compared to donor and acceptor, respectively ($PLQE_D$ and $PLQE_A$) through integrated kinetics. PM6 and blends' kinetics were plotted between 655 and 725 nm, whereas PCBM kinetics between 685 and 755 nm.

Samples	λ _{exc} (nm)	τ _{avg,D} (ps)	PLQE _D (%)	PLQE _A (%)
PM6		197.2 ± 5.6		
РСВМ		442.1 ± 44.2		
PM6:PCBM		109.2 ± 3.2	44.7 ± 1.8	75.3 ± 7.9
PM6:PCBM/Ag	450 ^a	70.2 ± 2.9	64.4 ± 3.2	84.1 ± 9.1
PM6:PCBM/Ag + AA		54.4 ± 1.2	72.4 ± 2.6	86.2 ± 9.0
PM6:PCBM/Au		60.9 ± 1.9	69.1 ± 2.9	86.2 ± 9.0
PM6:PCBM/Au + AA		51.4 ± 1.2	73.9 ± 2.7	88.4 ± 9.0
PM6		155.7 ± 12.9		
РСВМ	532 ^b	398.1 ± 16.2		
PM6:PCBM		63.5 ± 2.7	59.2 ± 5.5	84.0 ± 4.9
PM6:PCBM/Ag		50.2 ± 2.0	67.7 ± 6.2	87.4 ± 5.0

At this excitation:

^a donor and acceptor should be equally excited,

^b more PM6 than PCBM should be excited, only a few samples were measured as no major differences were observed.



Fig. S19. Transient absorption spectra at different time delays of the nanoparticles dispersions after 532 nm excitation, fluence 11.7 μ J cm⁻²: **a**, PM6:PCBM, **b**, PM6:PCBM/Ag, **c**, PM6:PCBM/Au. **d**, **e**, The corresponding kinetics of PM6 hole polaron (PM6⁺) probed at 757 – 758 nm and 890 – 900 nm, respectively.

PM6:Y6-based photocatalyst



Fig. S20. Normalized TRPL spectra (averaged from ~0 to 2 ns) of nanoparticles dispersions: **a**, neat PM6 (black) and neat Y6 (red), **b**, PM6:Y6, **c**, PM6:Y6/Ag, **d**, PM6:Y6/Ag + ascorbic acid (AA), **e**, PM6:Y6/Au and **f**, PM6:Y6/Au + AA, with λ_{exc} = 450 (darker colour), 532 and 780 nm (lighter colour). Note: for 780 nm excitation (~145 nJ/cm²) an 808 nm long-pass filter (LP808) was used, therefore, the emission is slightly cut around that wavelength (clearer in panel b). The excitation pulse at 780 nm is still going through the long-pass filter (clearer in panel b).

Table S5. Averaged lifetimes and PL quenching efficiencies compared to donor and acceptor, respectively ($PLQE_D$ and $PLQE_A$). PM6 kinetics were plotted between 655 and 725 nm, whereas Y6 and blends kinetics between 820 and 890 nm. A long component (longer than PM6) can be seen in the PM6 blends upon 450 and 532 nm excitation.

Samples	λ _{exc} (nm)	τ _{avg} (ps)	PLQE _D (%)	PLQE _A (%)
PM6		197.2 ± 5.6		
Y6		278.8 ± 5.4*		
PM6:Y6		100.1 ± 3.3	49.2 ± 2.1	64.1 ± 2.4
PM6:Y6/Ag	450	79.6 ± 7.9	59.7 ± 6.2	71.4 ± 7.2
PM6:Y6/Ag + AA		90.8 ± 1.4	54.0 ± 1.8	67.4 ± 1.8
PM6:Y6/Au		82.5 ± 1.5	58.2 ± 2.0	70.4 ± 1.9
PM6:Y6/Au + AA		91.1 ± 1.3	53.8 ± 1.8	67.3 ± 1.7
PM6		155.7 ± 12.9		
Y6	520 a	313.2 ± 7.4		
PM6:Y6	552	85.7 ± 3.8	44.9 ± 4.2	72.6 ± 3.7
PM6:Y6/Ag		76.0 ± 3.0	51.1 ± 4.7	75.7 ± 3.5
Y6		-	339.1 ± 29.9	
PM6:Y6	780 ^b	-	76.0 ± 7.3	77.6 ± 10.1
PM6:Y6/Ag		-	78.6 ± 7.3	76.8 ± 9.8

* A monoexponential fit was used in this case.

At this excitation:

^a more PM6 than Y6 should be excited, only a few systems were measured since no major differences were observed in $PLQE_D$.

^b only Y6 should be excited, only a few systems were measured since no major differences were observed in PLQE_{A.}



Fig. S21. Transient absorption spectra at different time delays of the nanoparticles dispersions after 532 nm excitation, fluence 31 μ J cm⁻²: **a**, PM6:Y6, **b**, PM6:Y6/Ag, **c**, PM6:Y6/Au. The corresponding kinetics of the ground state photobleaching (PB) of **d**, PM6, and **e**, Y6. **f**, The corresponding kinetics of Y6 electron polaron (Y6⁻) probed at 920 – 950 nm.



Fig. S22. Photoinduced absorption spectra of PM6:Y6 NPs suspensions with and without metal cocatalysts (absorbance 0.26, 1 mm pathlength) following 515 nm excitation (1.93 W cm⁻²).

PCE10:ITIC-based photocatalyst



Fig. S23. Normalized TRPL spectra (averaged from ~0 to 2ns) of nanoparticles dispersions: **a**, neat PCE10 (black) and ITIC (red), **b**, PCE10:ITIC, **c**, PCE10:ITIC/Ag, **d**, PCE10:ITIC/Au, **e**, PCE10:ITIC/Ag + ascorbic acid (AA), and **f**, PCE10:ITIC/Au + AA, with λ_{exc} = 650 nm at 0.3 nJ/cm².

Table S6. Averaged lifetimes and PL quenching efficiencies compared to donor and acceptor, respectively ($PLQE_D$ and $PLQE_A$) The kinetics were plotted for the range shadowed in Figure S23, in grey PCE10 and blends and in red ITIC.

Samples	λ _{exc} (nm)	τ _{avg} (ps)	PLQE _D (%)	PLQE _A (%)
PCE10		92.9 ± 1.6		
ΙΤΙϹ		238.9 ± 6.9		
PCE10:ITIC		81.5 ± 1.6	12.3 ± 0.3	65.9 ± 2.3
PCE10:ITIC/Ag	650	73.4 ± 1.3	17.8 ± 0.4	68.0 ± 2.3
PCE10:ITIC/Ag + AA		38.1 ± 1.2	59.0 ± 2.2	84.0 ± 3.7
PCE10:ITIC/Au		59.0 ± 1.4	36.5 ± 1.1	75.3 ± 2.8
PCE10:ITIC/Au + AA		46.7 ± 1.1	49.7 ± 1.5	80.4 ± 3.0



Fig. S24. Transient absorption spectra at different delay times of the nanoparticles dispersions after 532 nm excitation, fluence 11.7 μ J cm⁻²: **a**, PCE10:ITIC, **b**, PCE10:ITIC/Ag, **c**, PCE10:ITIC/Au. The corresponding kinetics of **d**, PCE10⁺ (cation), and **e**, ITIC⁻ (anion).



Fig. S25. Photoinduced absorption spectra of PCE10:ITIC NPs suspensions with and without metal cocatalysts (absorbance 0.33, 1 mm pathlength) following 660 nm excitation (1.92 W cm⁻²): **a**, in the visible wavelength spectral region, **b**, in the NIR wavelength spectral region.

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