

Electronic Supplementary Information

Size-Dependent Exciton Dynamics in TADF Nanoparticles for Efficient CO₂

Photoreduction

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Table S1 Summary of particle size and distribution from DLS

Preparation parameters and variables	Average particle size and distribution from DLS (nm)
SDS–0.4 wt%, 300 seconds at 100% amplitude	40.3
SDS–0.3 wt%, 300 seconds at 100% amplitude	66.2
SDS–0.2 wt%, 300 seconds at 100% amplitude	83.5
SDS–0.05 wt%, 120 seconds at 100% amplitude	107.5
SDS–0.04 wt%, 120 seconds at 100% amplitude	124.8
SDS–0.03 wt%, 120 seconds at 100% amplitude	133.7
SDS–0.02 wt%, 120 seconds at 100% amplitude	145.4
SDS–0.02 wt%, 60 seconds at 100% amplitude	154.6
SDS–0.01 wt%, 120 seconds at 100% amplitude	167.6
SDS–0.01 wt%, 60 seconds at 100% amplitude	177.9
SDS–0.01 wt%, 60 seconds at 95% amplitude	190.1
SDS–0.006 wt%, 60 seconds at 90% amplitude	211.4

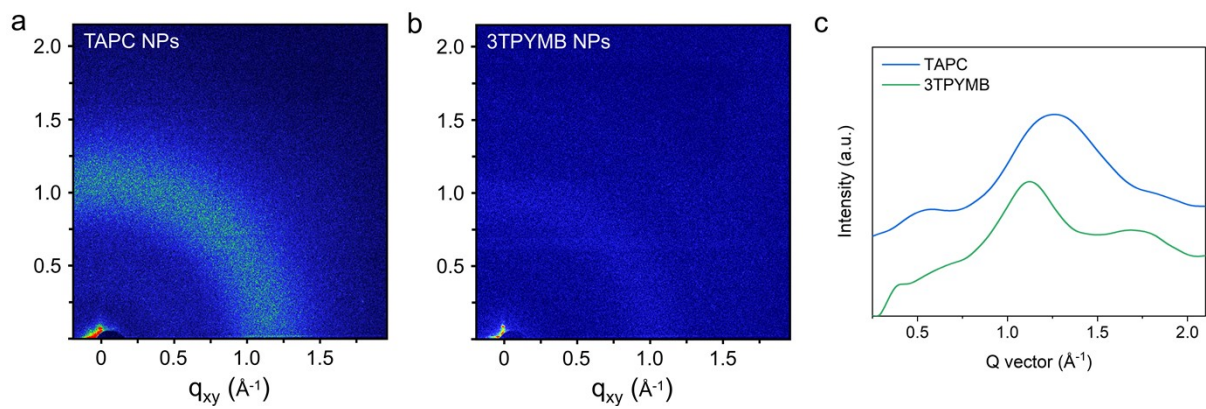


Fig. S1 2D GIWAXS patterns of (a) TAPC nanoparticles, (b) 3TPYMB nanoparticles. (c) Corresponding 1D profiles derived from these patterns.

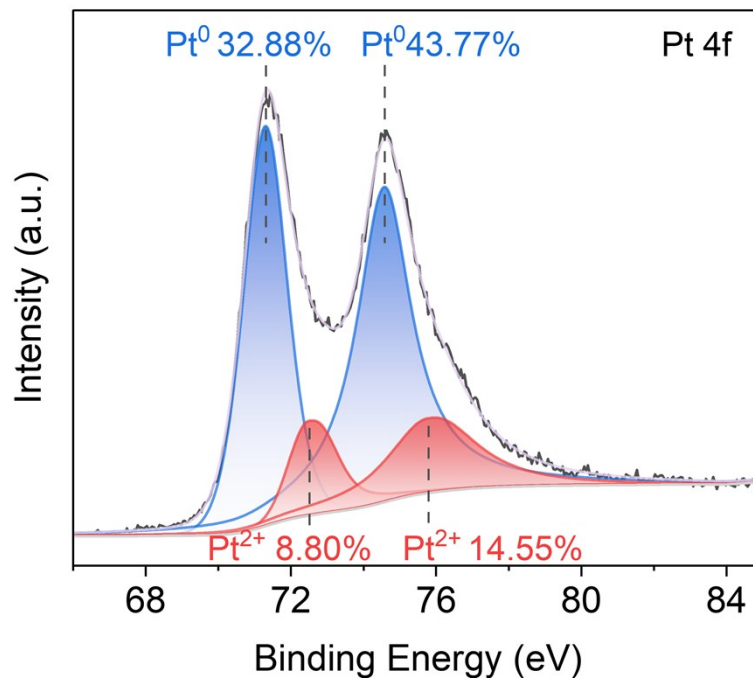


Fig. S2 Pt 4f XPS spectrum of TAPC:3TPYMB NPs after in situ Pt photodeposition.

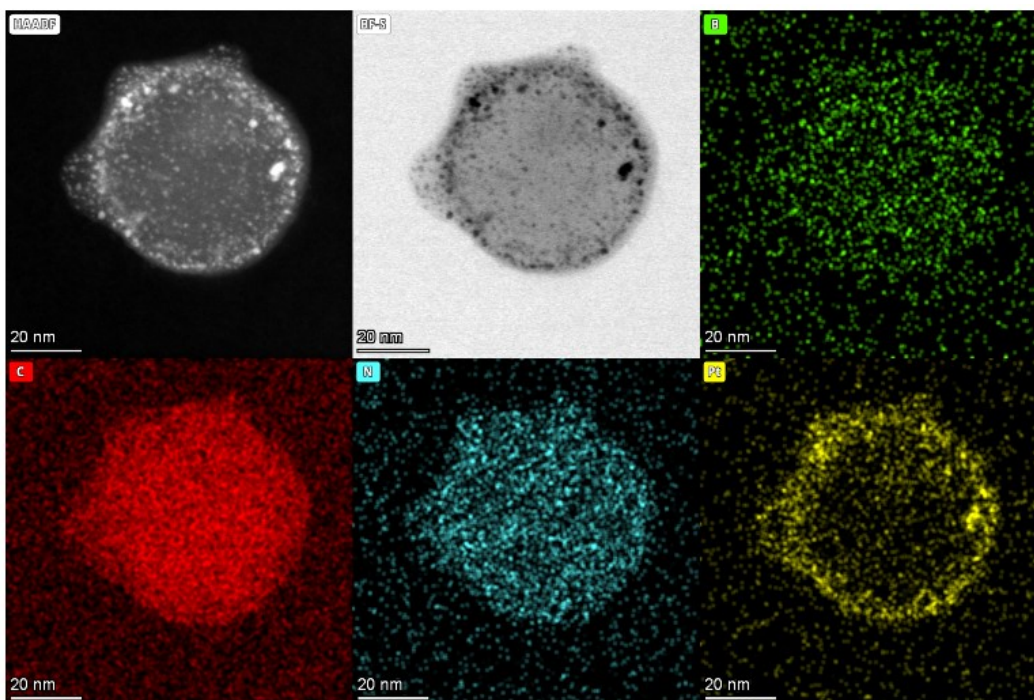


Fig. S3 HAADF STEM image and elemental mapping of TAPC:3TPYMB NPs after in situ Pt photodeposition, including B, C, N, and Pt distributions.

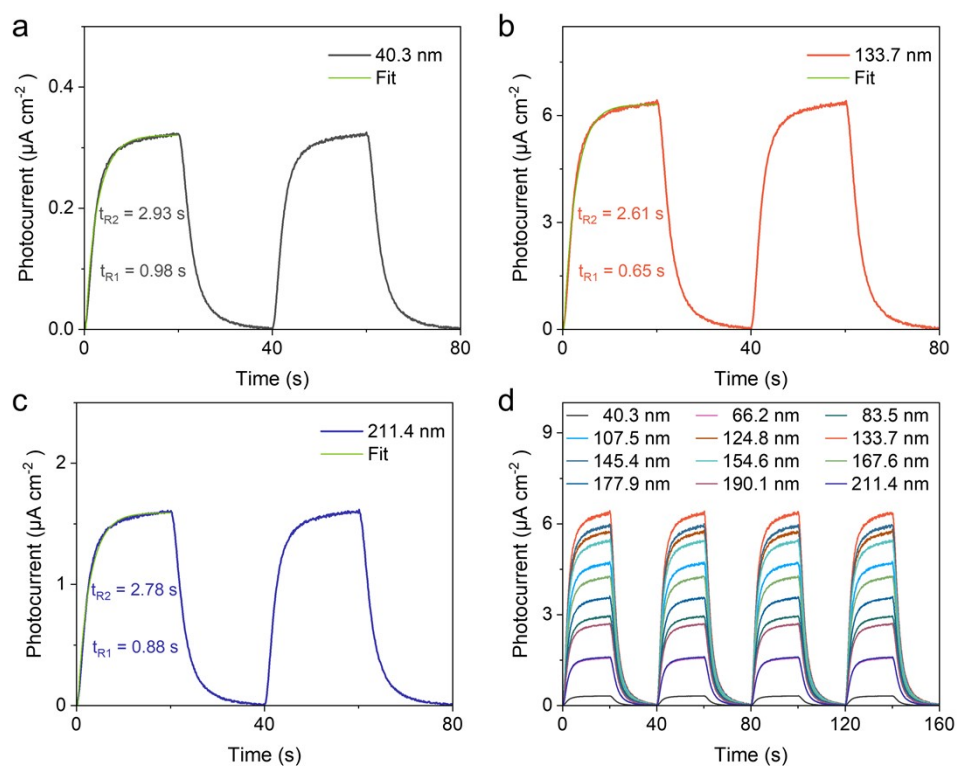


Fig. S4 Biexponential fitting of the photocurrent rise process for TAPC:3TPYMB NPs with sizes of (a) 40.3 nm, (b) 133.7 nm, and (c) 211.4 nm. The fitted rise time constants are indicated in each panel. Transient photocurrent responses of TAPC:3TPYMB NPs over the full particle-size range under intermittent light irradiation. (d) Current density vs. time of NP films in 0.1 M TEOA solution, the 365 nm LED is employed for illumination (50 mW cm^{-2}). The TAPC:3TPYMB molar ratio was 4:6.

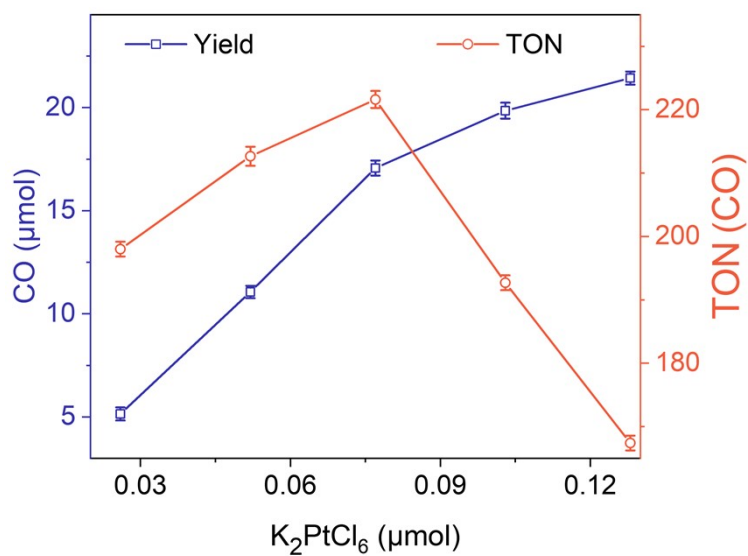


Fig. S5 Effect of K_2PtCl_6 amount on the photocatalytic CO_2 reduction performance of TAPC:3TPYMB NPs. Reaction conditions: total catalytic solution volume = 5 mL, TAPC:3TPYMB NPs, 9.78 μM ; TEOA, 0.1 M; 365 nm LED irradiation; reaction time, 18 h.

Table S2 Comparison of photocatalytic CO₂ reduction performance with reported organic and Pt containing systems

Catalyst /Photosensitizer	Sacrificial agent	Solvent	Rate (mmol·g ⁻¹ ·h ⁻¹)/TON	Light Irradiation / time	Ref
Pt (0.077 μM) TAPC-3TPYMB (9.78 μM)	TEOA	H₂O (5 mL)	CO: 68.7 TON: 241.4	LED@365nm 18 h	This Work
FeTotpy (10 μM) 4CzIPN (50 μM)	TEA	DMF (5 mL)	CO: 167.5 TON: 244	LED@420–650nm 3 h	1
FeL ^{MeOH} (50 μM) 4-DPAIPN (400 μM)	DIPEA	ACN / TFE (5 mL)	CO: 295.5 TON: 1112	1 sun 7 h	2
Co(oTMPyP) (5 μM) 4P-DPAIPN (500 μM)	Ascorbate	NaHCO ₃ buffer (4mL)	CO: 96.4 TON: 2700	LED@450nm 21 h	3
[Zn(cztpy) ₂] ²⁺ (10 μM) 4CzIPN (100 μM)	TEA	DMA/H ₂ O (5 mL)	CO: 19.5 TON: 116	LED@420nm 6 h	4
[Ru(ttpy) ₂](PF ₆) ₂ (20 μM) 4CzIPN (100 μM)	TEA	CH ₃ CN/H ₂ O (5 mL)	CO: 53.9 TON: 124	LED@420–650nm 2 h	5
Mn (50 μM) 3DPAFIPN (250 μM)	TEOA/BIH	DMA (2mL)	CO: 56.1 TON: 538	LED@440nm 20 h	6
[Fe(qpy)(OH ₂) ₂] ²⁺ (50 μM) NPs-23k (20 μM)	TEA/BIH	CH ₃ CN/H ₂ O (5mL)	CO: 282.1 TON: 2041	Xenon lamp (λ > 400 nm) 18 h	7
Pt (200 mg) C-In ₂ O ₃ (4 mg)	TEOA	H ₂ O (200 mL)	CO: 0.633 TON: 3.165 CH ₄ : 0.140	Xe lamp 5 h	8
Pt-BiOBr (20 mg) Pt-BiOBr (20 mg)	None	H ₂ O (0.1 mL)	CO: 0.094 TON:/	Xe lamp 3 h	9
Fe(qpy) (20 μM) mpg-C ₃ N ₄ (8 mg)	TEOA	CH ₃ CN (4 mL)	CO:22.7 TON: 155	Hg lamp 17 h	10
Pt-CdS/ZnS (4mg) CdS/ZnS	TEOA	H ₂ O (15 mL)	CO: 0.094 CH ₄ :0.0374 TON:/	Xe lamp (λ ≥ 425 nm) 10 h	11
AuPt AuPt	None	H ₂ O (0.08 mL)	CO: 1.01 TON:/	Xe lamp /	12
Pt-SA/TiO ₂ -Ti ₃ C ₂ (50 mg) TiO ₂ -Ti ₃ C ₂	None	H ₂ O (5 mL)	CO: 0.02 TON: /	Xe lamp AM 1.5G 3 h	13

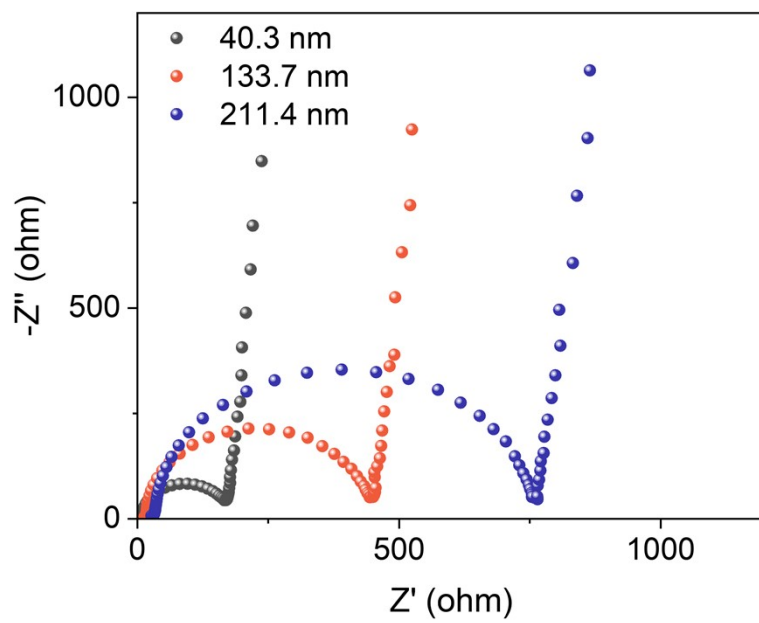


Fig. S6 EIS analysis of TAPC:3TPYMB nanoparticles with sizes of 40.3, 133.7, and 211.4 nm.

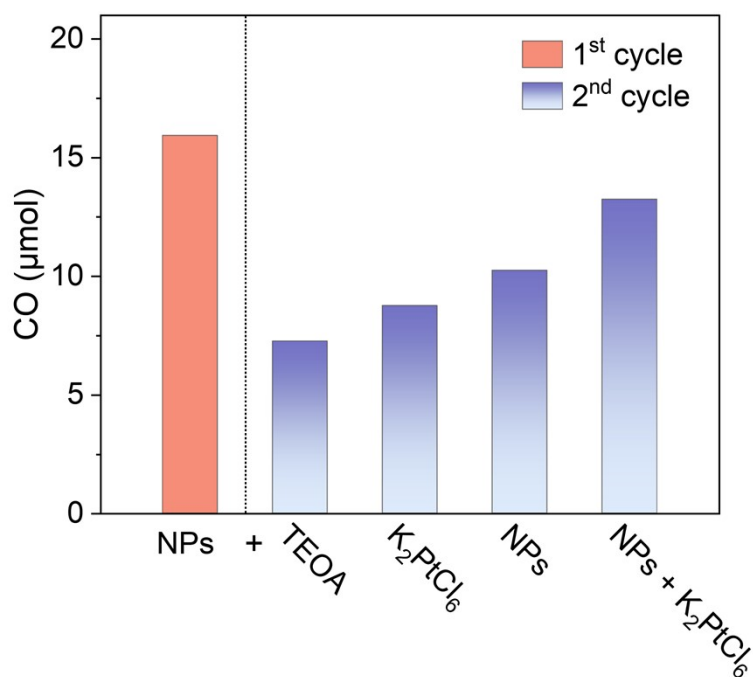


Fig. S7 Recycle experiments. CO₂ photoreduction was first performed in the presence of TAPC:3TPYMB NPs, K₂PtCl₆, and TEOA under 365 nm LED irradiation. After the first cycle, TEOA, K₂PtCl₆, NPs, or NPs + K₂PtCl₆ were added for the second cycle. The irradiation time of each cycle was 12 h. TAPC:3TPYMB NPs: 9.78 μM; K₂PtCl₆: 0.077 μM; TEOA: 0.1 M.

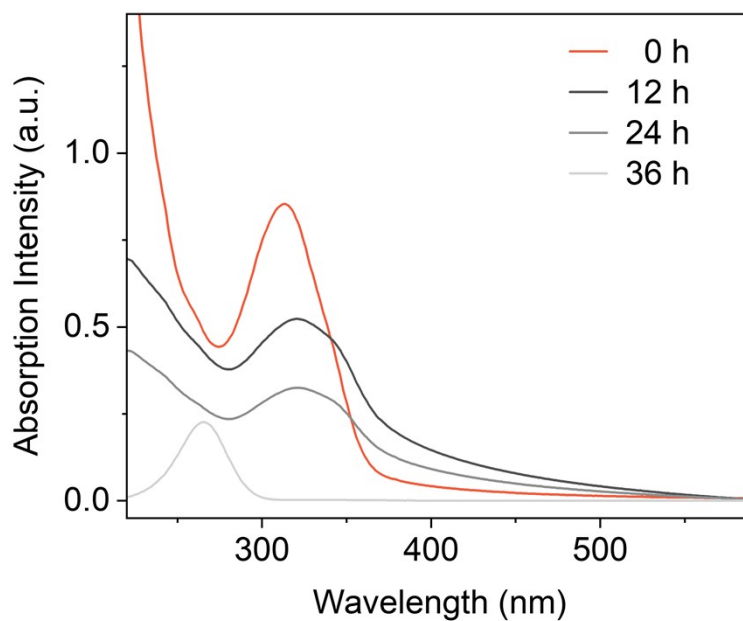


Fig. S8 UV-vis absorption spectra of TAPC:3TPYMB NPs were recorded before reaction and after different irradiation times. The spectra at 0, 12, 24, and 36 h correspond to the fresh sample, the sample after the first 12 h photocatalytic reaction, the sample after 24 h irradiation, and the sample after 36 h irradiation, respectively.

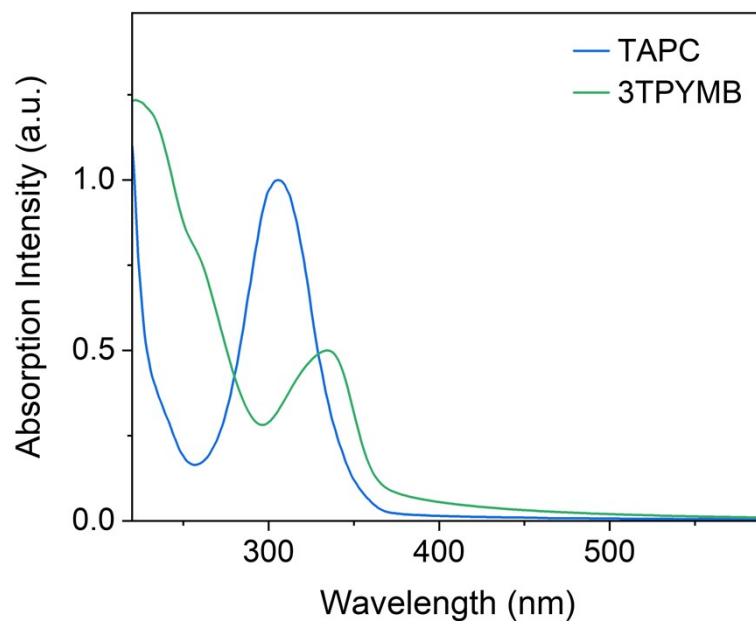


Fig. S9 UV-visible absorption spectra of TAPC and 3TPYMB nanoparticles.

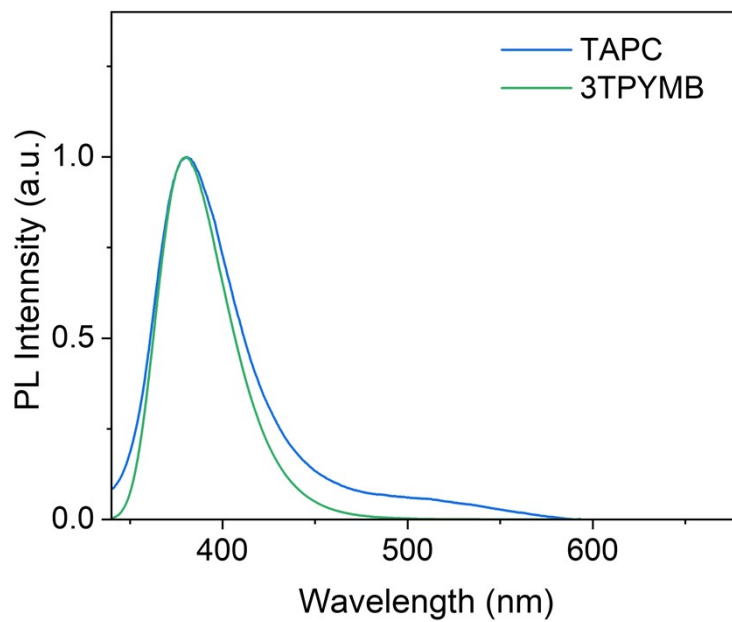


Fig. S10 Photoluminescence spectra of TAPC and 3TPYMB nanoparticles (excitation wavelength: 340 nm).

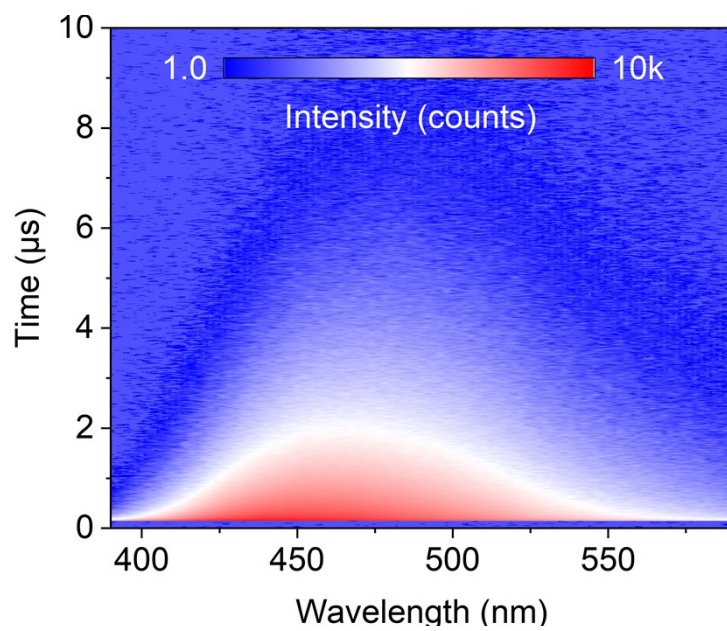


Fig. S11 Time resolved emission contour map of TAPC:3TPYMB nanoparticles.

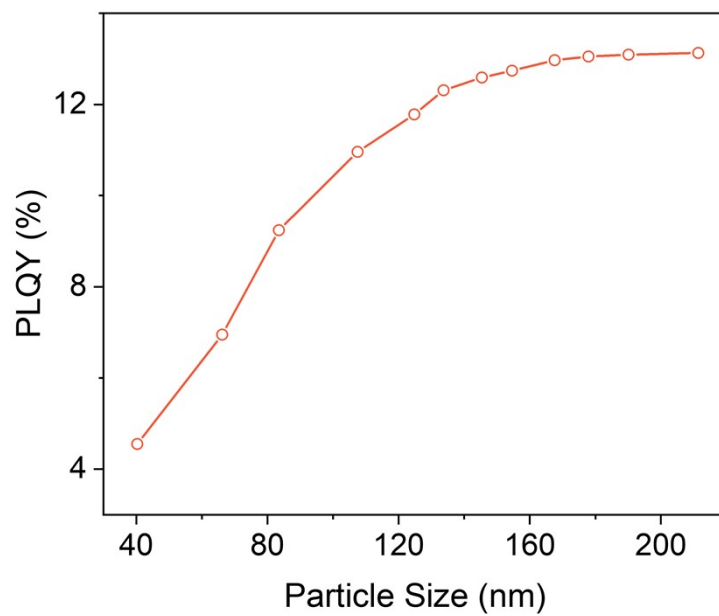


Fig. S12 PLQY values of TAPC:3TPYMB NPs with different particle sizes.

Table S3 Radiative decay rates of NPs with different particle sizes

Size (nm)	Φ (%)	Φ_{PF} (%)	Φ_{DF} (%)	τ_p (ns)	τ_d (ns)	k_r (10^5 s $^{-1}$)
40.3	4.55	0.82	2.15	58.70	270.49	1.41
66.2	6.95	1.57	4.40	61.64	355.28	2.55
83.5	9.24	1.97	6.74	83.25	394.69	2.37
107.5	10.96	2.12	6.90	84.99	599.73	2.49
124.8	11.78	2.37	8.46	88.34	587.40	2.68
133.7	12.31	3.22	8.52	88.06	632.44	3.65
145.4	12.59	3.71	8.53	94.68	653.25	3.92
154.6	12.74	3.65	8.75	95.50	669.44	3.83
167.6	12.97	3.79	8.87	102.68	675.25	3.69
177.9	13.05	3.52	8.83	107.83	714.80	3.26
190.1	13.09	3.95	8.80	110.47	742.39	3.57
211.4	13.13	4.49	8.44	124.68	764.25	3.60

We calculated the radiative decay rates (k_r) of TAPC:3TPYMB NPs using PLQY and fluorescence lifetime data. The transient PL decay curves were fitted with a three exponential function. The prompt fluorescence quantum yield (Φ_{PF}) and delayed fluorescence quantum yield (Φ_{DF}) were estimated from the total PL quantum yield (Φ_{PL}) and the integrated area fractions of the assigned prompt and delayed fluorescence components. The quantum yields and rate constants were calculated using the following equations according to the reported method.¹⁴

$$(1) \Phi_{PF} = \Phi_{PL}r_{PF}; r_{PF} = \tau_p A_2 / (\tau_1 A_1 + \tau_p A_2 + \tau_d A_3)$$

$$(2) \Phi_{DF} = \Phi_{PL}r_{DF}; r_{DF} = \tau_d A_3 / (\tau_1 A_1 + \tau_p A_2 + \tau_d A_3)$$

$$(3) k_r = \Phi_{PF} / \tau_p$$

where A_1 , A_2 , and A_3 are the fitted amplitudes of the minor, prompt, and delayed components, respectively.

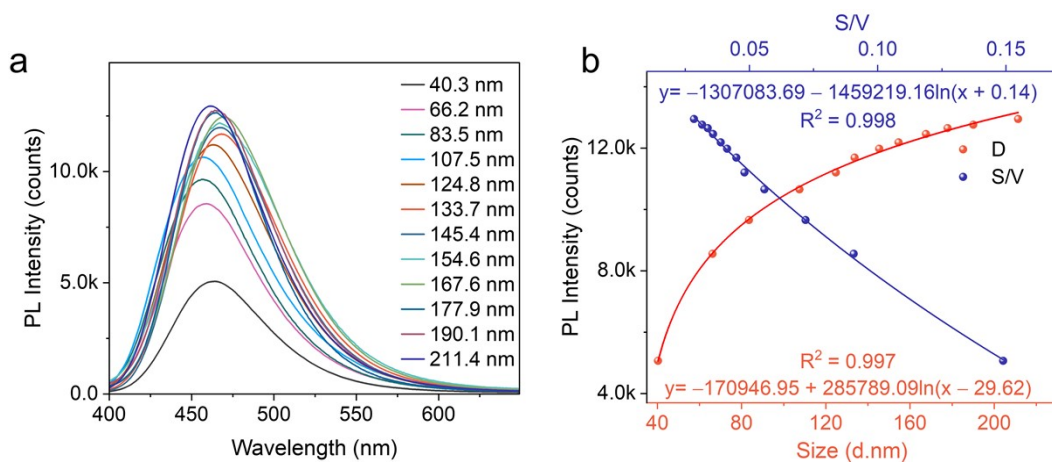


Fig. S13 (a) PL spectra of TAPC:3TPYMB NPs with different particle sizes. (b) Dependence of PL intensity and calculated surface area to volume ratio (S/V) on particle size.

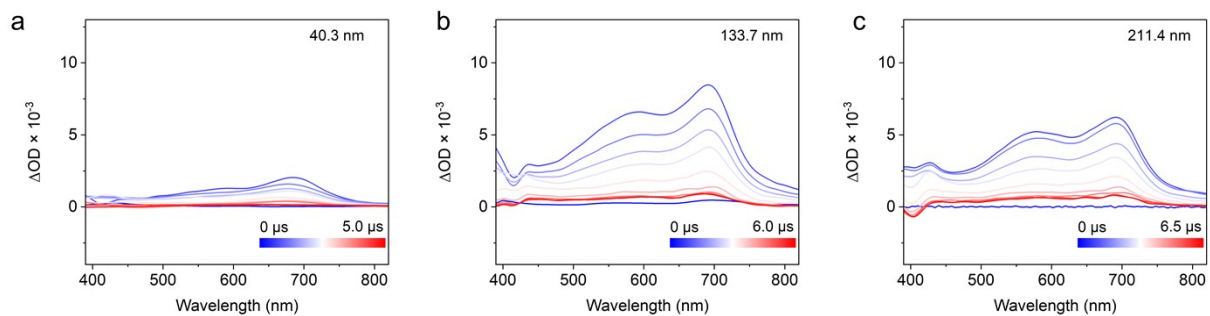


Fig. S14 (a-c) Transient absorption (TA) spectra of TAPC:3TPYMB (5:5) NPs (33.3 nm, 63.9 nm and 212.9 nm), excited at 340 nm.

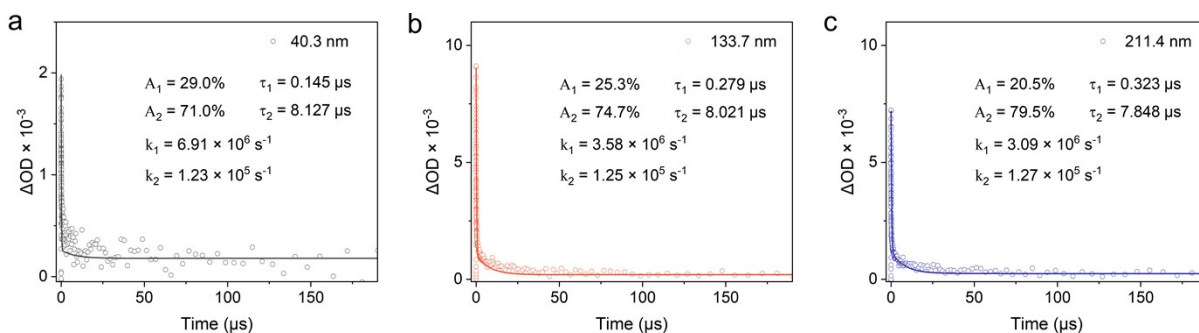


Fig. S15 Biexponential fitting of TA decay traces at 700 nm for TAPC:3TPYMB NPs with sizes of (a) 40.3 nm, (b) 133.7 nm, and (c) 211.4 nm.

In TAPC based exciplex systems, the transient absorption signal around 700 nm has been assigned to the absorption of the TAPC radical cation [TAPC]^{•+}.¹⁵ Therefore, in the present TAPC:3TPYMB system, the TA decay at 700 nm can be used to monitor the dynamics of CT related charge species. The decay traces were fitted using the following biexponential function:

$$\Delta OD(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

where τ_1 represents the fast decay process of CT related charge species, and τ_2 represents the slow decay process of long-lived CT related charge species. The corresponding apparent decay rate constants were calculated as $k_1 = 1/\tau_1$ and $k_2 = 1/\tau_2$.

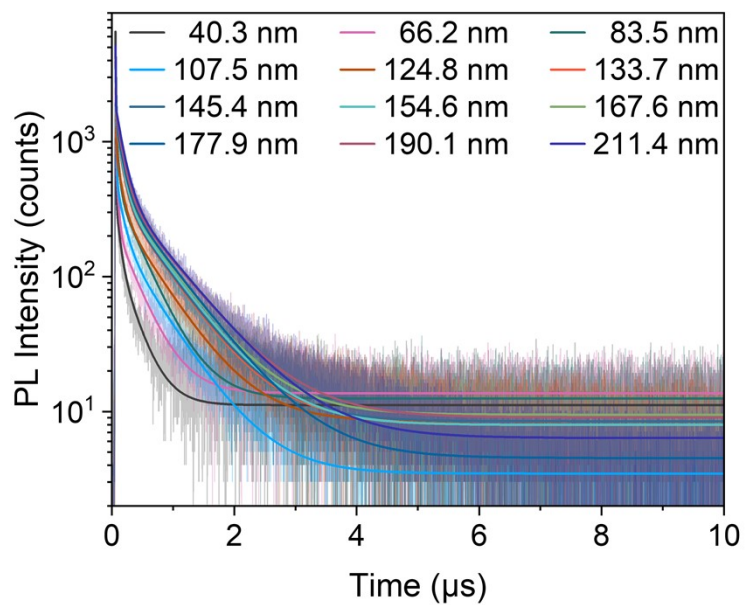


Fig. S16 Transient fluorescence decay curves for TAPC:3TPYMB (5:5) nanoparticles of varying sizes (excitation wavelength: 375 nm)

Table S4 Fitting parameters of transient fluorescence decay curves for TAPC:3TPYMB nanoparticles

Size (nm)	A ₁ (%)	τ ₁ (ns)	A ₂ (%)	τ ₂ (ns)	A ₃ (%)	τ ₃ (ns)	τ (ns)
40.3	34.61	4.60	18.13	58.70	47.26	270.49	140.07
66.2	14.00	4.09	22.66	61.64	63.35	355.28	239.60
83.5	5.74	3.72	21.31	83.25	72.95	394.69	305.88
107.5	17.70	8.94	19.33	84.99	62.97	599.73	395.66
124.8	8.14	5.50	20.08	88.34	71.78	587.40	439.82
133.7	4.66	4.72	26.13	88.06	69.21	632.44	460.92
145.4	2.81	3.01	29.46	94.68	67.73	653.25	470.40
154.6	2.63	2.95	28.68	95.50	68.69	669.44	487.30
167.6	2.39	2.87	29.21	102.68	68.40	675.25	491.92
177.9	5.35	7.23	26.97	107.83	67.68	714.80	513.26
190.1	2.62	3.68	30.14	110.47	67.24	742.39	532.59
211.4	1.52	2.40	34.21	124.68	64.28	764.25	533.92

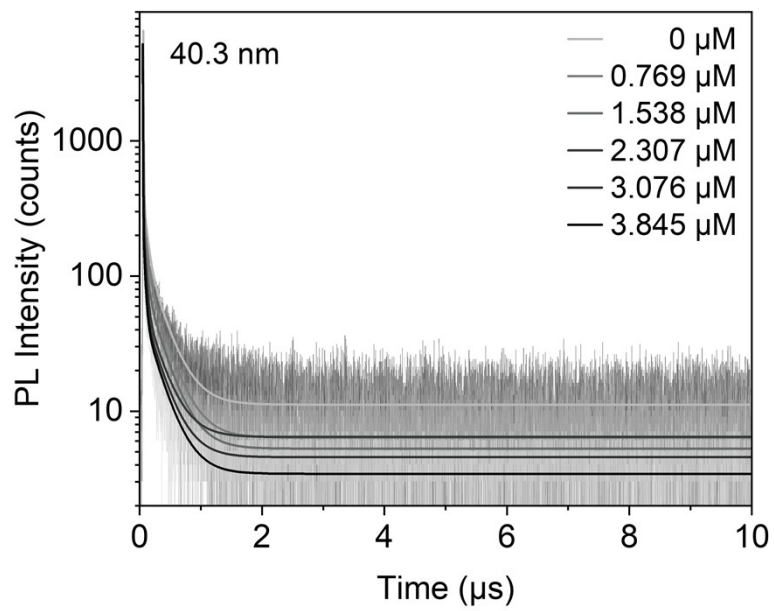


Fig.S17 Transient photoluminescence decay curves of 40.3 nm TAPC:3TPYMB (5:5) nanoparticles with varying concentrations of K_2PtCl_6 .

Table S5 Fitting parameters of transient fluorescence decay curves for 40.3 nm TAPC:3TPYMB nanoparticles under different K₂PtCl₆ Concentrations

K ₂ PtCl ₆ (μM)	A ₁ (%)	τ ₁ (ns)	A ₂ (%)	τ ₂ (ns)	A ₃ (%)	τ ₃ (ns)	τ (ns)
0	34.61	4.60	18.13	58.70	47.26	270.49	140.07
0.769	38.38	5.83	18.11	52.51	43.51	268.65	128.64
1.538	41.70	4.94	17.03	40.26	41.27	265.93	118.66
2.307	38.77	3.16	22.93	37.18	38.30	261.57	109.93
3.076	44.47	3.40	18.68	28.88	36.84	259.99	102.70
3.845	46.07	3.40	19.35	28.88	34.58	259.99	97.05

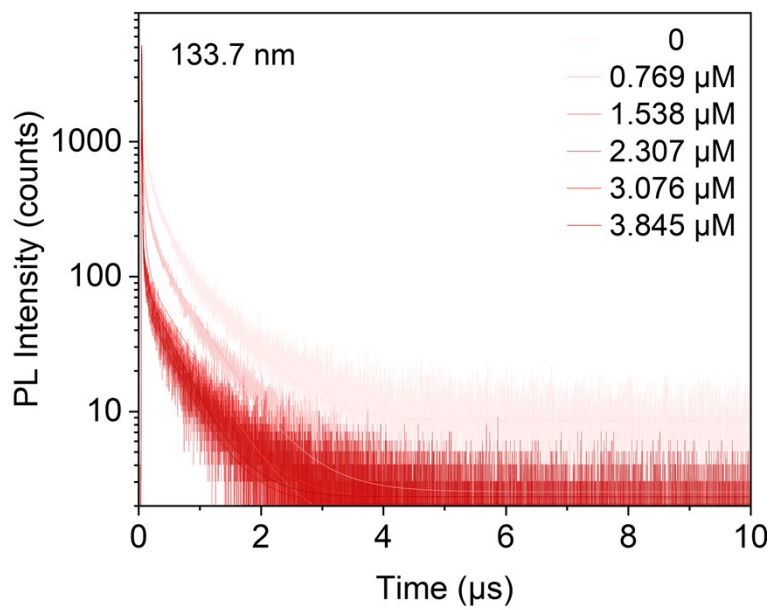


Fig.S18 Transient photoluminescence decay curves of 133.7 nm TAPC:3TPYMB (5:5) nanoparticles with varying concentrations of K_2PtCl_6 .

Table S6 Fitting parameters of transient fluorescence decay curves for 133.7 nm TAPC:3TPYMB nanoparticles under different K₂PtCl₆ Concentrations

K ₂ PtCl ₆ (μM)	A ₁ (%)	τ ₁ (ns)	A ₂ (%)	τ ₂ (ns)	A ₃ (%)	τ ₃ (ns)	τ (ns)
0	4.66	4.72	26.13	88.06	69.21	632.44	460.92
0.769	11.86	5.41	23.38	69.92	64.76	598.98	404.90
1.538	24.61	7.72	13.12	50.44	62.27	571.60	364.44
2.307	30.17	4.44	9.34	45.47	60.49	537.27	330.60
3.076	36.45	4.68	5.98	40.00	57.57	504.94	294.77
3.845	34.96	4.44	10.81	45.47	54.22	487.27	270.68

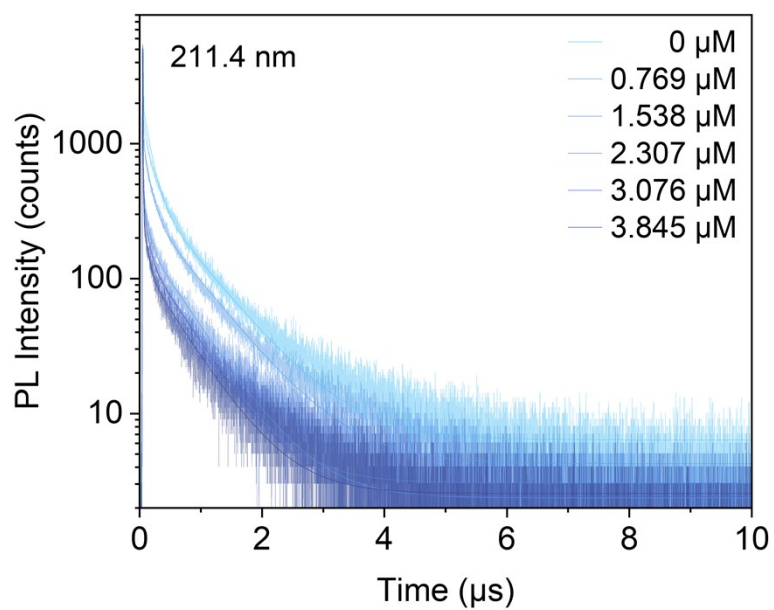


Fig.S19 Transient photoluminescence decay curves of 211.4 nm TAPC:3TPYMB (5:5) nanoparticles with varying concentrations of K_2PtCl_6 .

Table S7 Fitting parameters of transient fluorescence decay curves for 211.4 nm TAPC:3TPYMB nanoparticles under different K₂PtCl₆ Concentrations

K ₂ PtCl ₆ (μM)	A ₁ (%)	τ ₁ (ns)	A ₂ (%)	τ ₂ (ns)	A ₃ (%)	τ ₃ (ns)	τ (ns)
0	1.52	2.40	34.21	124.68	64.28	764.25	533.92
0.769	6.14	5.31	25.99	104.75	67.87	711.38	510.35
1.538	11.17	3.89	13.51	66.88	75.32	627.14	481.82
2.307	11.96	3.47	14.24	65.39	73.80	608.39	458.71
3.076	15.64	4.27	14.02	65.95	70.33	602.93	433.98
3.845	20.52	4.61	12.47	61.37	67.02	595.80	407.88

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