

Supporting Information

Charge Transfer Excitons in Un-Functionalized Graphite Wrapped MAPbBr₃ Nanocrystal Composite with Different Morphologies

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1. Instrumental details

1.1 UV Vis Absorption Spectroscopy and Photoluminescence Spectroscopy

Shimadzu UV-Vis 2450 spectrophotometer was used for recording UV-Vis absorption spectra in the range of 200-650 nm. Photoluminescence spectra were taken by Horiba scientific Fluoromax-4C spectrophotometer. A quartz cuvette of 10 mm path length and volume 4 ml was used for collecting data.

1.2 Field Emission Scanning Electron Microscopy (FEI-SEM)

SEM images, EDX, and mapping had been done on model FE-SEM Quanta 200 FEG and Zeiss Gemini SEM.

1.3 Transmission Electron Microscopy (TEM)

TEM study was done by FEI TECHNAI G2 20 S-TWIN. A drop of diluted samples was deposited on a carbon-coated copper grid. Again, a drop was added after drying it, and drying was carried at ambient temperature.

1.4 Powder XRD

P-XRD was carried out on Bruker -D8 Advance having Target Cu and accelerating voltage 40kV from 5 to 50° at the rate of 2°/min.

1.5 TCSPC studies

Fluorescence lifetime decay measurements were recorded on a 1 cm quartz cell on a Horiba Jobin Yvon Fluorocube Fluorescence Lifetime System equipped with Nano LEDs and LDs as the excitation source and an automated polarization accessory (Model 5000 U-02).

1.6 Transient absorption spectroscopy (TAS) studies

The spectral and kinetic studies have been done by ultrafast transient absorption spectroscopy. The experimental setup of ultrafast transient absorption spectroscopy (UFTS) or pump-probe technique is shown in fig.1. The UFTS setup is based on a Ti: sapphire laser (Coherent Micra). It is used to generate mode-locked Gaussian-shaped pulses of pulse width ~ 35 fs and repetition rate 80MHz centered around 800nm. The high energy beam part was further amplified via an optical parametric amplifier (OPA)(TOPAS) and converted into desired excitation wavelength or further called Pump. A silicon-based detector placed at far-field use to detect a change in intensity of the probe beam. The optical chopper at frequency 500Hz placed between the sample and detector to measure the difference in absorption (ΔA). ΔA sample profile concerning spectra wavelength (λ), and delay (τ) get on output. The wavelengths were measured with uncertainty ± 0.1 nm via ocean optics

spectrometer over a range of wavelength 400nm–800nm. For transient analysis, 420nm pump wavelength was used to excite the ground state, and a 450nm-790nm visible broad band probe was used.

1.7 Photoluminescence quantum yield

Absolute quantum yields were measured directly by using Edinburgh instrument FLS980.

1.8 X-Ray Photoelectron Spectroscopy (XPS)

Thin-film of perovskites has been studied on XPS with model no. PHI 5000 Versa Probe III for surface analysis.

Synthetic details

Synthesis of P100 and P100@G: For P100, we have taken 11.1 mg of MABr and 36.7 mg of PbBr_2 , which were dissolved in 1 mL of DMF with 100 μL of oleic acid and 100 μL oleylamine. Then we have added 30 μL of precursor solution into 3 mL of chloroform. We have centrifuged this solution at 7000 rpm speed for 10 minutes and again redisperse in chloroform, which was further used for characterizations.

We have added 60 mg of graphite into 10 mL chloroform (0.6% w/v in chloroform) to synthesize the perovskite NC/Graphite nanocomposite. We have sonicated it for 5 min so that graphite can disperse in chloroform. Then 30 μL precursor of P100 was mixed with the graphite solution to form the desired nanocomposite and mentioned as P100@G.

Synthesis of P150 and P150@G: For P150, we have taken 11.1 mg of MABr and 36.7 mg of PbBr_2 and dissolved the halide salts in 1 mL of DMF with 100 μL of oleic acid and 150 μL oleylamine. Then we have added 30 μL of precursor solution into 3 mL of chloroform. We have centrifuged this solution at 7000 rpm speed and again redisperse in chloroform, which was further used for characterizations.

We have added 60 mg of graphite into 10 mL chloroform (0.6% w/v in chloroform) to synthesize the perovskite NC/Graphite nanocomposite. We have sonicated it for 5 min so that graphite can disperse in chloroform. Then 30 μL precursor of P150 was mixed with the graphite solution to form the desired nanocomposite and mentioned as P150@G.

Synthesis of P200 and P200@G: For P200, we have taken 11.1 mg of MABr and 36.7 mg of PbBr_2 and dissolved them in 1 mL of DMF with 100 μL of oleic acid and 200 μL oleylamine.

Then we have added 30 μL of precursor solution into 3 mL of chloroform. We have centrifuged this solution at 7000 rpm speed and again redisperse in chloroform, which was further used for characterizations.

We have added 60mg of graphite into 10mL chloroform (0.6% w/v in chloroform) to synthesize the perovskite NC/Graphite nanocomposite. We have sonicated it for 5 min so that graphite can disperse in chloroform. Then 30 μL precursor of P200 was mixed with the graphite solution to form the desired nanocomposite and was mentioned as P200@G.

Synthesis of P250 and P250@G: For P250, we have taken 11.1 mg of MABr and 36.7 mg of PbBr_2 dissolved in 1 mL of DMF with 100 μL of oleic acid and 250 μL oleylamine. Then we have added 30 μL of precursor solution into 3mL of chloroform. We have centrifuged this solution at 7000 rpm speed and again redisperse in chloroform, which was further used for characterizations.

We have added 60 mg of graphite into 10 mL chloroform (0.6% w/v in chloroform) to synthesize the perovskite NC/Graphite nanocomposite. We have sonicated it for 5 min so that graphite can disperse in chloroform. Then 30 μL precursor of P250 was mixed with the graphite solution to form the desired nanocomposite and mentioned as P250@G.

Synthesis of P300 and P300@G: For P300, we have taken 11.1 mg of MABr and 36.7 mg of PbBr_2 dissolved in 1 mL of DMF with 100 μL of oleic acid and 300 μL oleyl amine. Then we have added 30 μL of precursor solution into 3 mL of chloroform. We centrifuged this solution at 7000 rpm speed and redispersed it in chloroform, further used for characterizations. We have added 60 mg of graphite into 10 mL chloroform (0.6% w/v in chloroform) to synthesize the perovskite NC/Graphite nanocomposite. We have sonicated it for 5 min so that graphite can disperse in chloroform. Then 30 μL precursor of P300 was mixed with the graphite solution to form the desired nanocomposite and mentioned as P300@G.

Table S1. The difference in 2 theta value and FWHM of a) Pristine MAPbBr₃ b) Composite.

a)

Position [°2Th.]	Height [cts]	FWHM	d-spacing [Å]	Rel. Int. [%]
15.3884	90043.93	0.1968	5.75817	100
21.6374	3431.46	0.1968	4.10724	3.81
30.6148	58794.13	0.1968	2.92024	65.29
34.2516	5393.3	0.2165	2.61804	5.99
43.6068	1979.43	0.1968	2.07563	2.2
46.4124	3632.99	0.2165	1.95649	4.03

b)

Position [°2Th.]	Height [cts]	FWHM	d-spacing [Å]	Rel. Int. [%]
15.0788	10335.43	0.2362	5.87571	34.21
21.4554	1426.56	0.3936	4.14167	4.72
26.7913	30211.47	0.3542	3.32767	100
30.5267	6127.51	0.3936	2.92847	20.28
34.0738	2452.46	0.3149	2.6313	8.12
43.3495	924.62	0.9446	2.08735	3.06
46.2117	819.61	0.3936	1.96452	2.71

Table S2. Relative PLQY for **P35**.

	Graphite solution (mL)	PL Intensity	PL Intensity (%)	Quantum Yield (%)
P35	0	26.246*10 ⁵	100	51
	0.5	5.943*10 ⁵	22	17
	1.0	2.272*10 ⁵	9	9
	1.5	1.306*10 ⁵	5	6
	2.0	0.821*10 ⁵	3	3
P100	0	76.175*10 ⁵	100	53
	0.5	22.239*10 ⁵	29	19
	1.0	9.388*10 ⁵	12	9
	1.5	6.003*10 ⁵	8	5
	2.0	3.794*10 ⁵	5	2
P150	0	20.817*10 ⁵	100	29
	0.5	6.008*10 ⁵	29	7
	1.0	3.165*10 ⁵	15	3
	1.5	1.984*10 ⁵	9	2
	2.0	1.496*10 ⁵	7	1
P200	0	23.995*10 ⁵	100	26
	0.5	10.671*10 ⁵	44	7
	1.0	6.515*10 ⁵	27	3
	1.5	4.895*10 ⁵	20	1
	2.0	3.898*10 ⁵	16	0.5
P250	0	18.091*10 ⁵	100	16
	0.5	7.457*10 ⁵	41	3
	1.0	5.059*10 ⁵	28	2
	1.5	3.991*10 ⁵	22	0.73
	2.0	2.781*10 ⁵	15	0.4
P300	0	8.352*10 ⁵	100	5
	0.5	1.540*10 ⁵	18	2
	1.0	0.715*10 ⁵	8	0.76
	1.5	0.545*10 ⁵	6	0.44
	2.0	0.449*10 ⁵	5	0.32

Table S3. TAS details for the **P35** and **P300** samples and their corresponding composite sample.

Sample name	Wavelength h	t_1 (ps)	A_1 (%)	t_2 (ps)	A_2 (%)	t_3 (ps)	A_3 (%)
P35	488.7	13.6	-0.756	2410	-0.244	inf	0
	518.2	87.9	0.771	1870	0.229	inf	0
	537.2	7.05	-0.846	2130	-0.154	inf	0
	745.4	45.7	-0.869	5800	-0.131	inf	0
P35G	471.0	1430	-0.0825	39.6	-0.0165	0.187	-0.901
	483.4	1620	-0.449	1490	0.423	0.187	0.108
	512.3	0.41	-0.266	0.38	-0.205	0.361	0.529
P300	489.3	145	0.725	1920	0.275	inf	0
	510.5	2.94	-0.496	116	-0.383	5130	-0.121
P300G	493.4	11700	-0.128	28.8	-0.39	0.428	-0.482
	502.2	2.83	-0.485	26800	-0.0988	19.7	-0.416

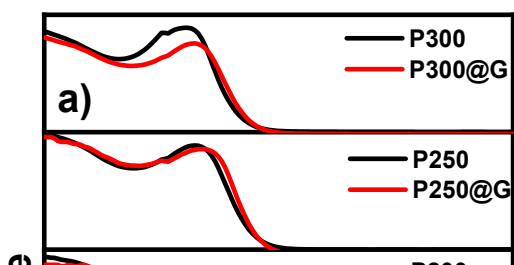


Fig. S1. Absorption studies of pure and composite samples.

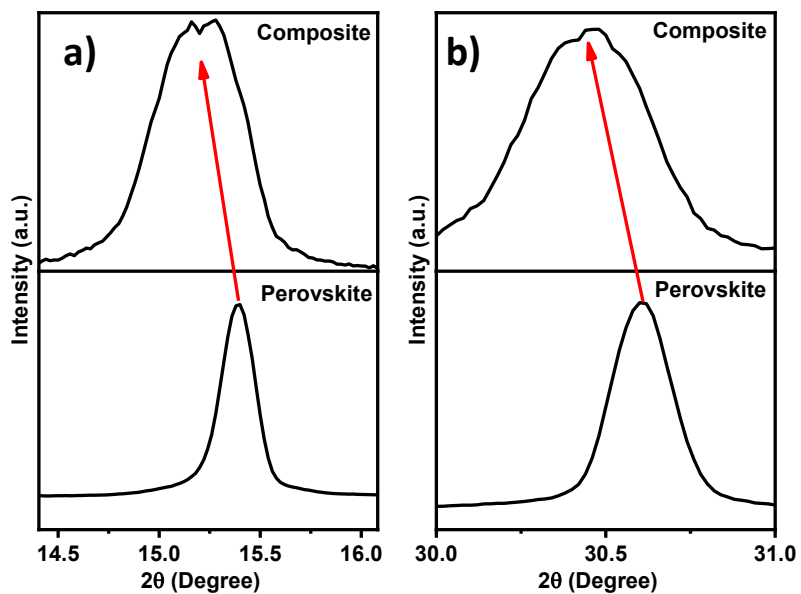
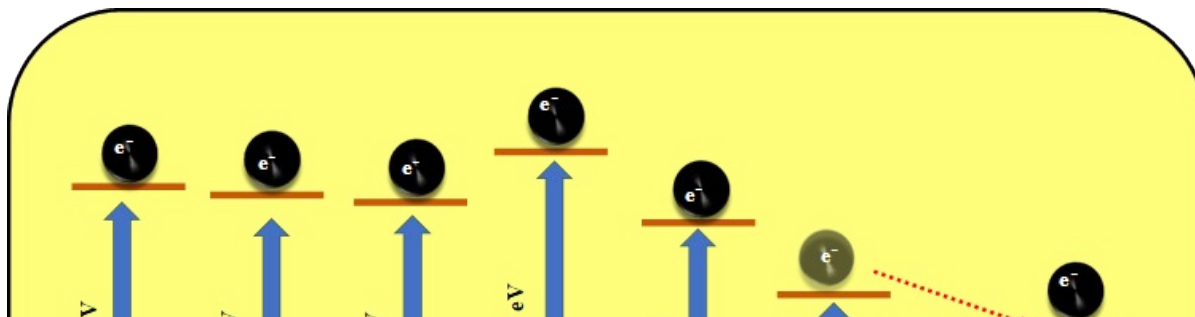


Fig. S2 Enlarged area of peak situated at 15 degrees and 30 degrees for pristine perovskite and corresponding composite.



Scheme S1: Schematic representation of CTE generation.

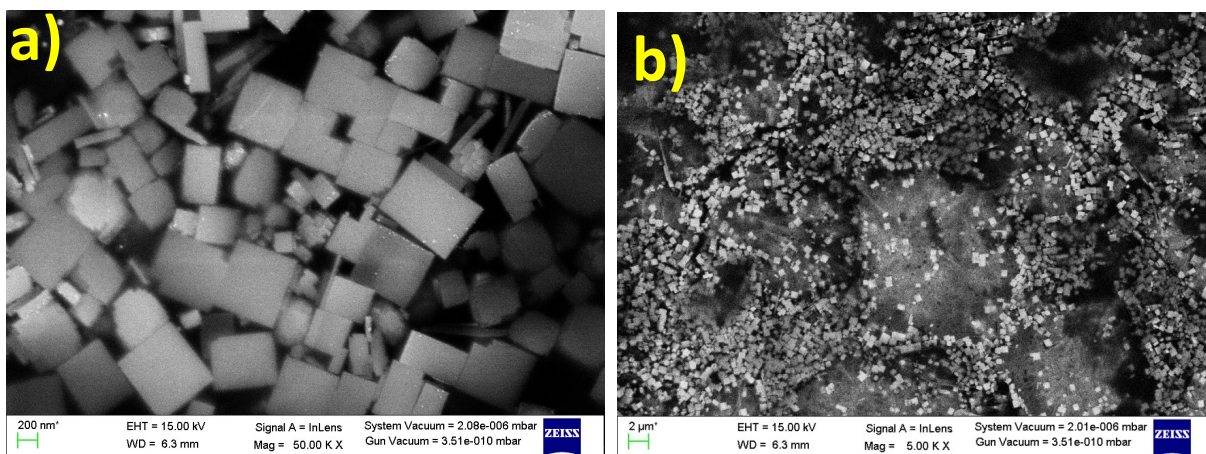


Fig. S3.1. SEM images of Pristine MAPbBr₃ Nanocrystals with 35 μL oleyl amine at a) 200 nm and b) 2 μm scale bar.

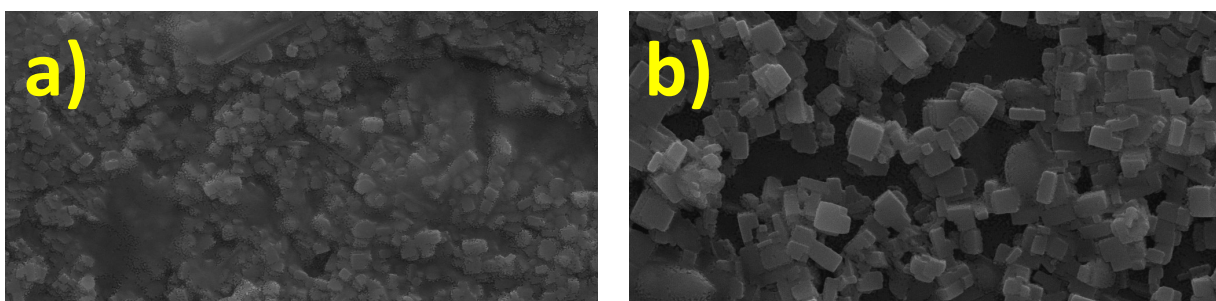


Fig. S3.2. SEM images of Pristine MAPbBr₃ Nanocrystals with 100 μ L oleyl amine at a) 5 μ m and b) 2 μ m scale bar.

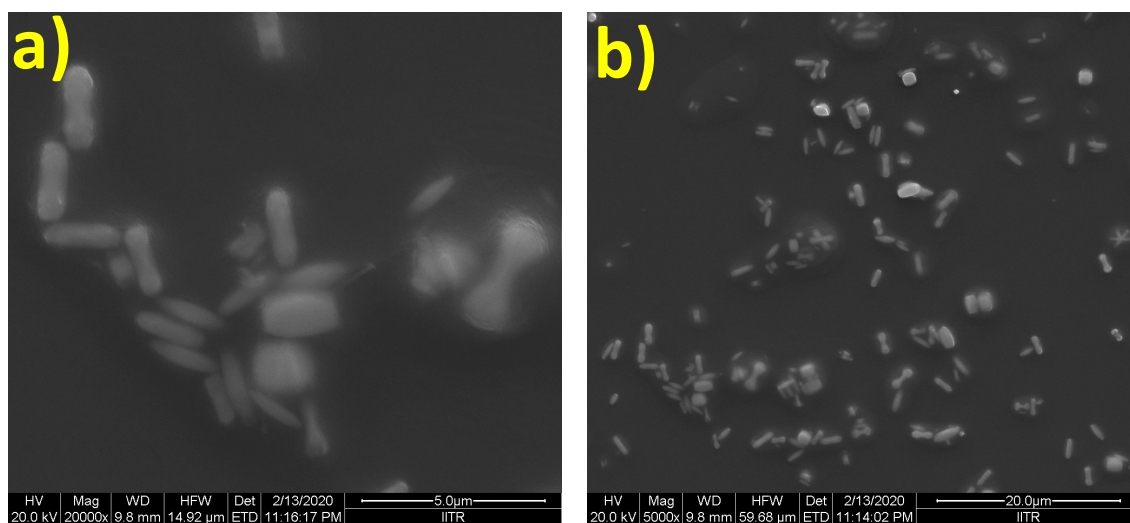


Fig. S3.3. SEM images of Pristine MAPbBr₃ Nanocrystals with 150 μ L oleyl amine at a) 5 μ m and b) 20 μ m scale bar.

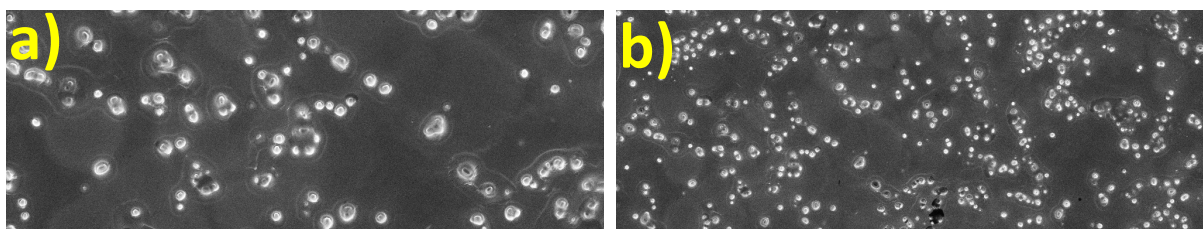


Fig. S3.4. SEM images of Pristine MAPbBr₃ Nanocrystals with 200 μ L oleyl amine at a) 2 μ m and b) 10 μ m scale bar.

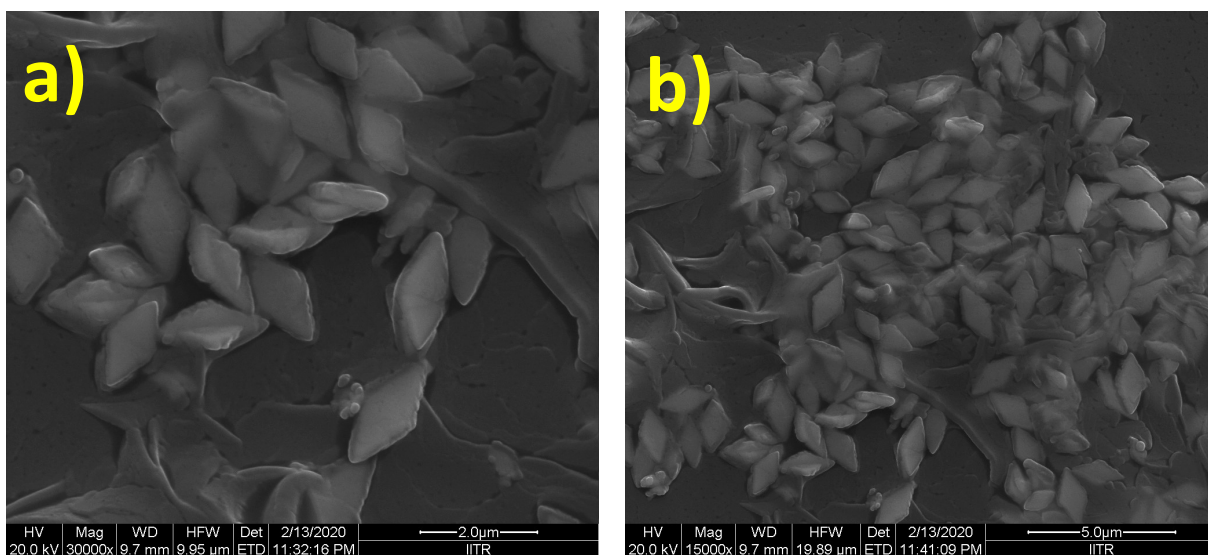


Fig. S3.5. SEM images of Pristine MAPbBr₃ Nanocrystals with 250 μ L oleyl amine at a) 2 μ m and b) 5 μ m scale bar.

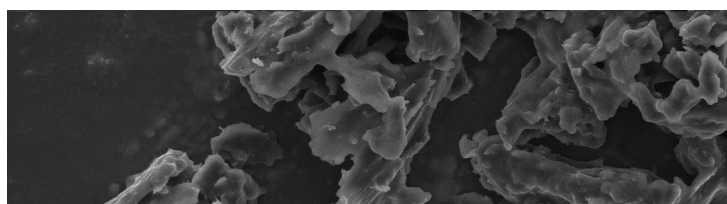


Fig. S3.6. SEM images of graphite.

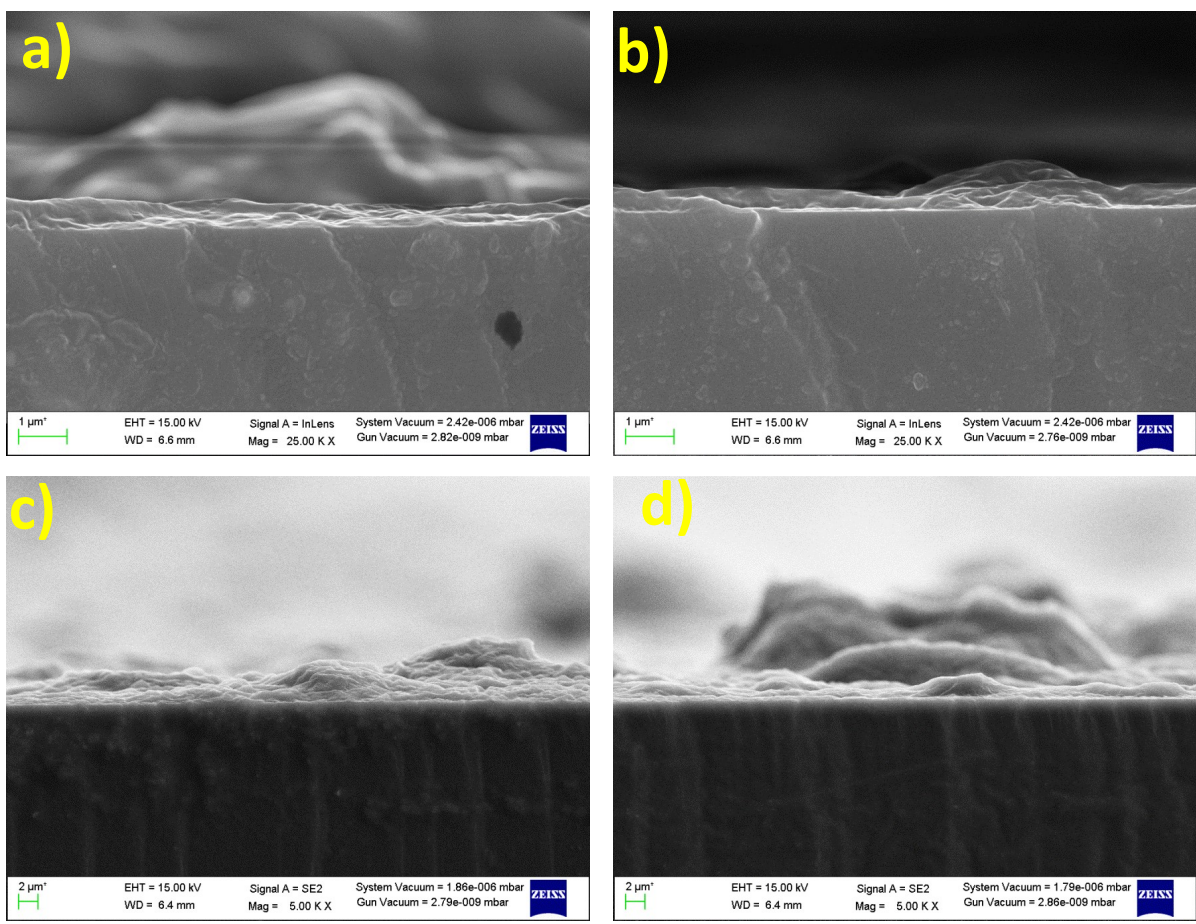


Fig. S4.1. Cross-section SEM images of a) Pristine MAPbBr₃ Nanocrystals with 35 μL oleyl amine. b) Perovskite-Graphite composite with 35 μL oleylamine. c) Pristine MAPbBr₃ Nanocrystals with 100 μL oleyl amine. d) Perovskite-Graphite composite with 100 μL oleyl amine.

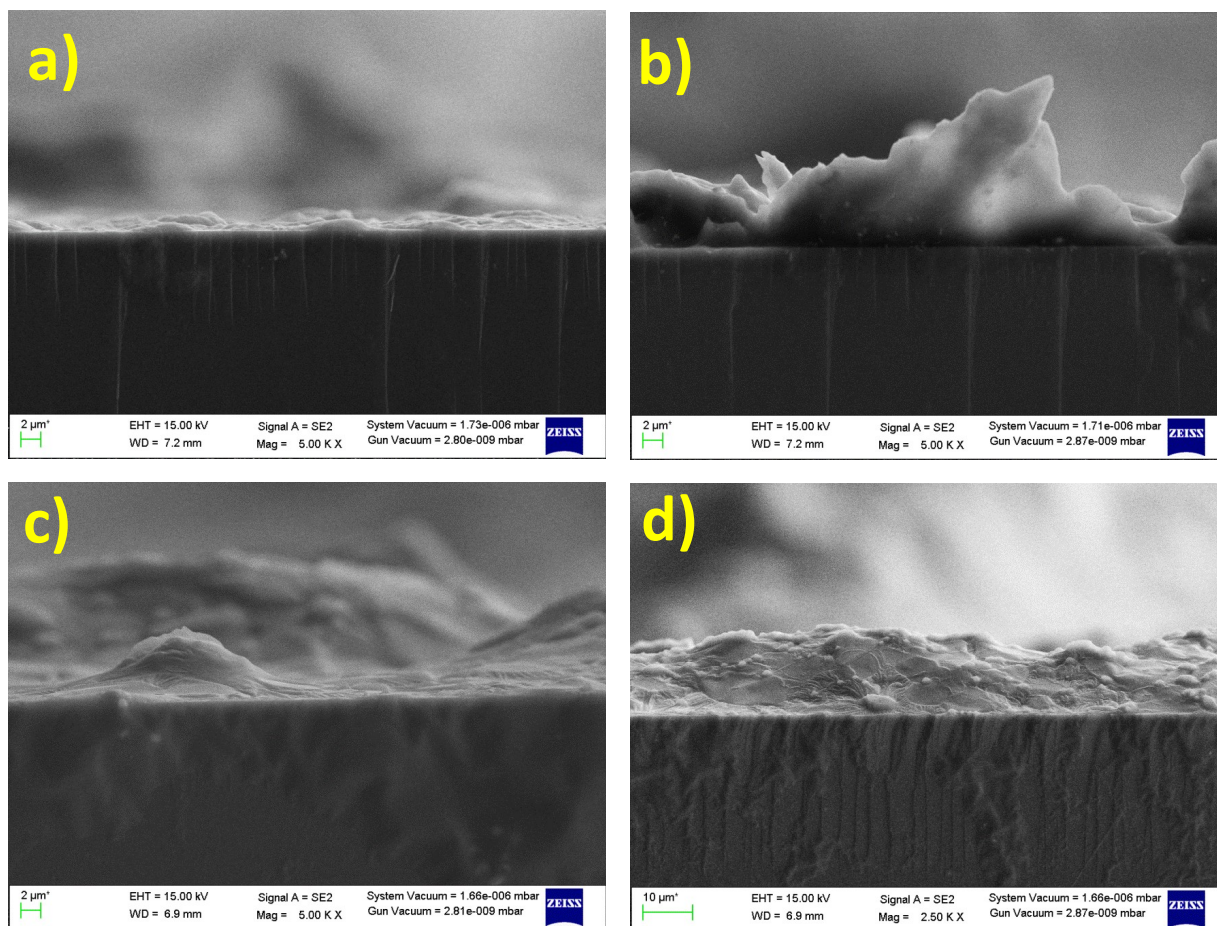


Fig. S4.2. Cross-section SEM images of a) Pristine MAPbBr₃ Nanocrystals with 150 μL oleyl amine. b) Perovskite-Graphite composite with 150 μL oleyl amine. c) Pristine MAPbBr₃ Nanocrystals with 200 μL oleyl amine. d) Perovskite-Graphite composite with 200 μL oleyl amine.

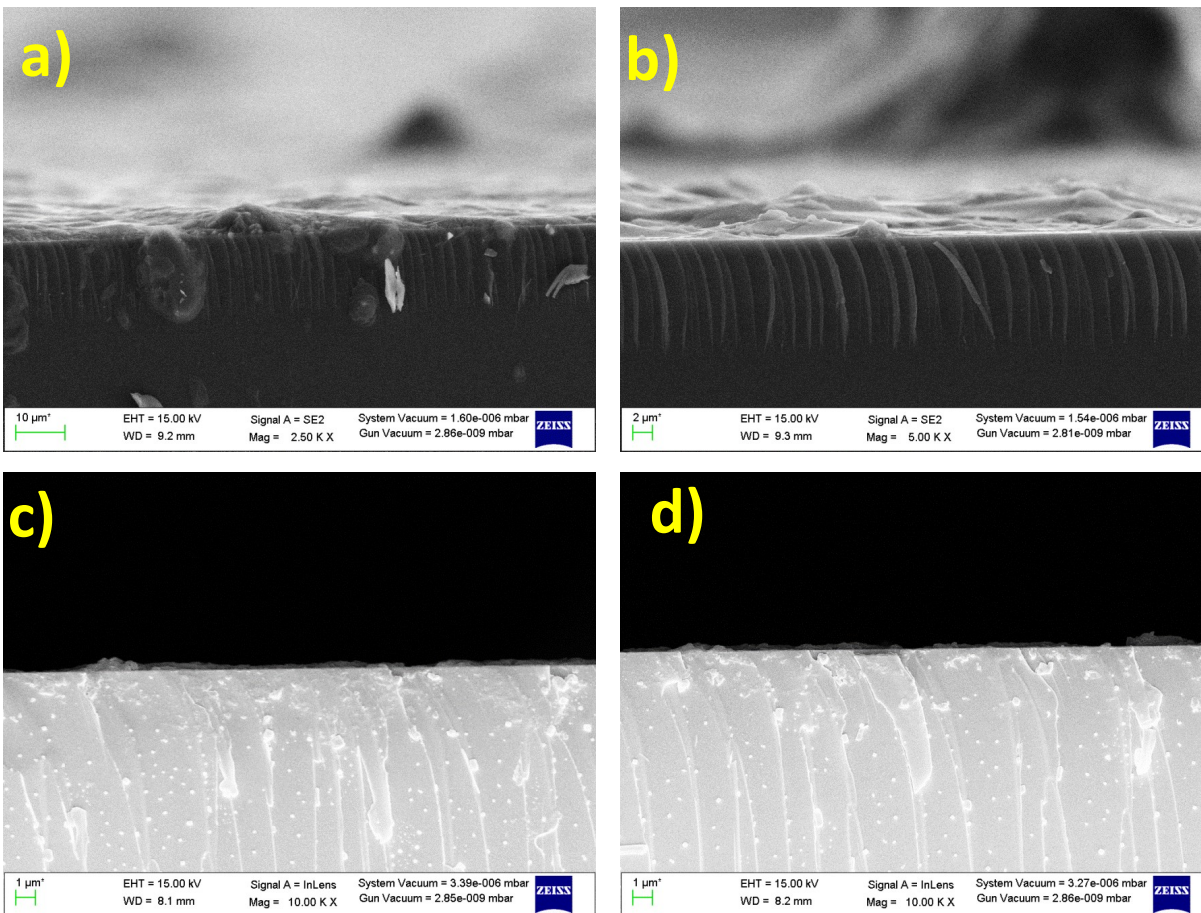


Fig. S4.3. Cross-section SEM images of a) Pristine MAPbBr₃ Nanocrystals with 250 μL oleyl amine, b) Perovskite-Graphite composite with 250 μL oleyl amine c) Pristine MAPbBr₃ Nanocrystals with 300 μL oleyl amine d) Perovskite-Graphite composite with 300 μL oleyl amine

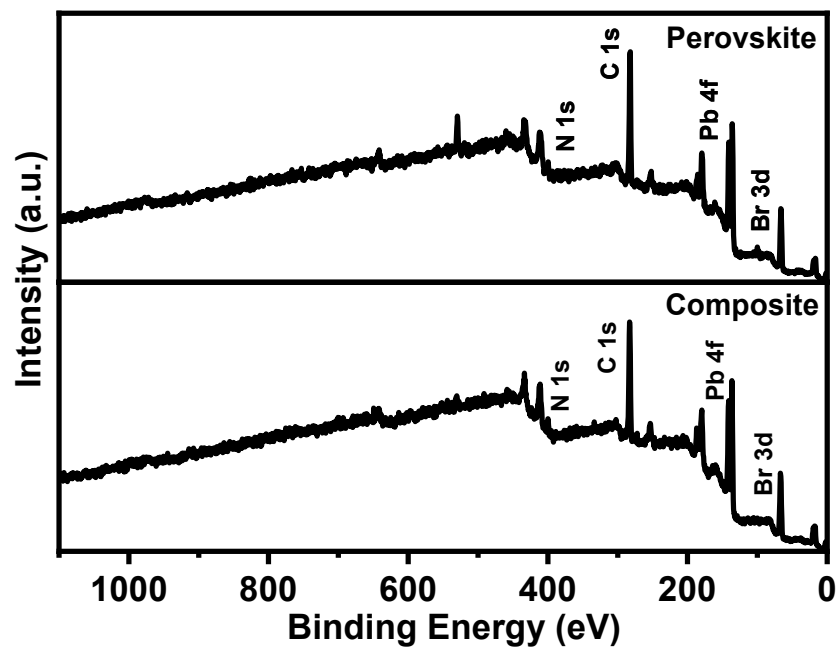


Fig. S5 XPS survey scan of Pristine perovskite and composite with graphite.

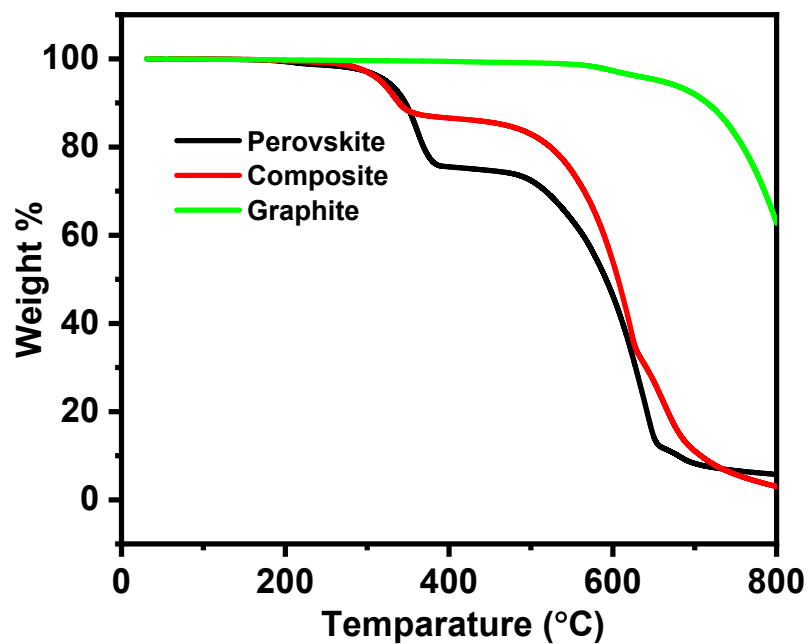


Fig. S6 TGA spectrum of Pristine perovskite and composite with graphite.

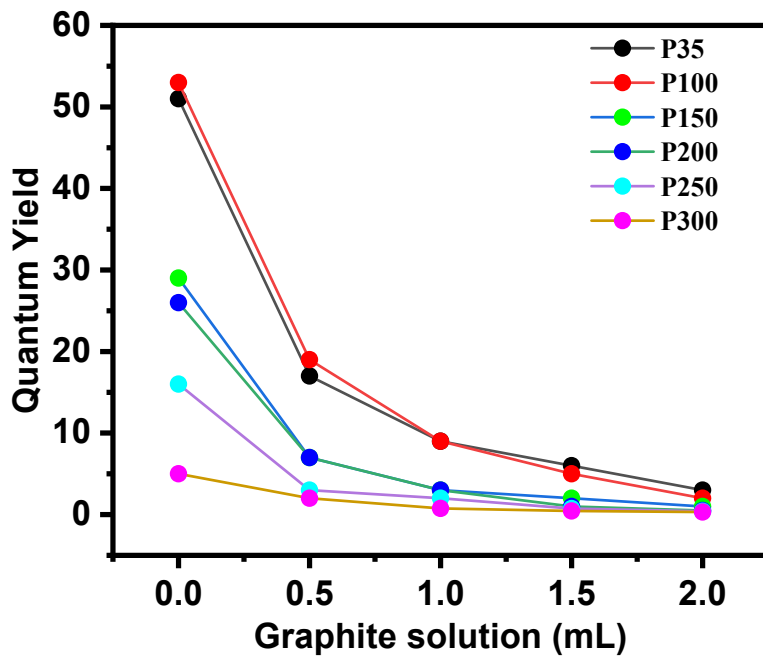


Fig. S7 Photoluminescence quantum yield of P35 to P300 with varying amount of graphite.

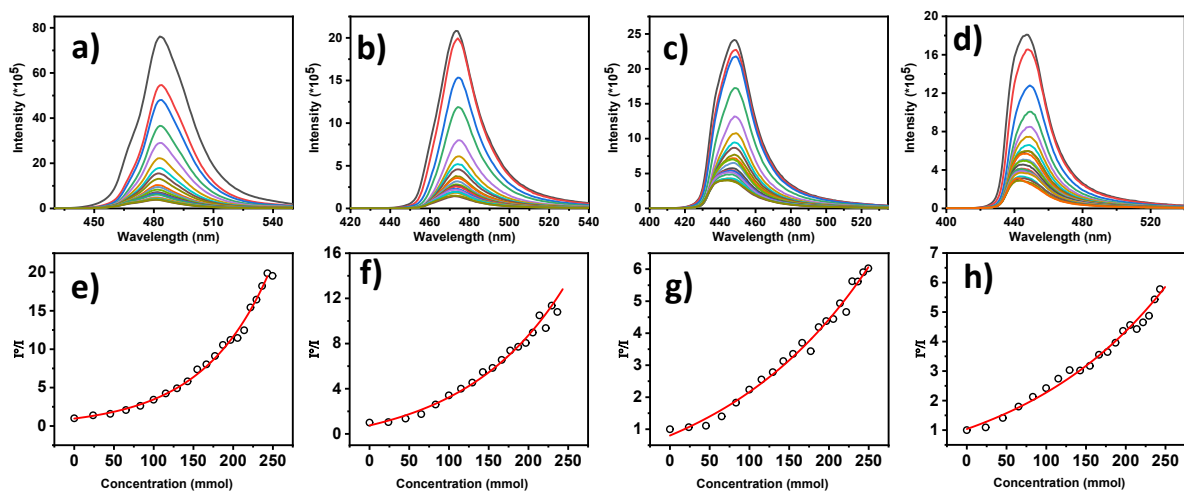


Fig. S8. Photoluminescence quenching of a) P100 b) P150 c) P200 d) P250. Respective intensity vs concentration graphs of e) P100 f) P150 g) P200 h) P250.

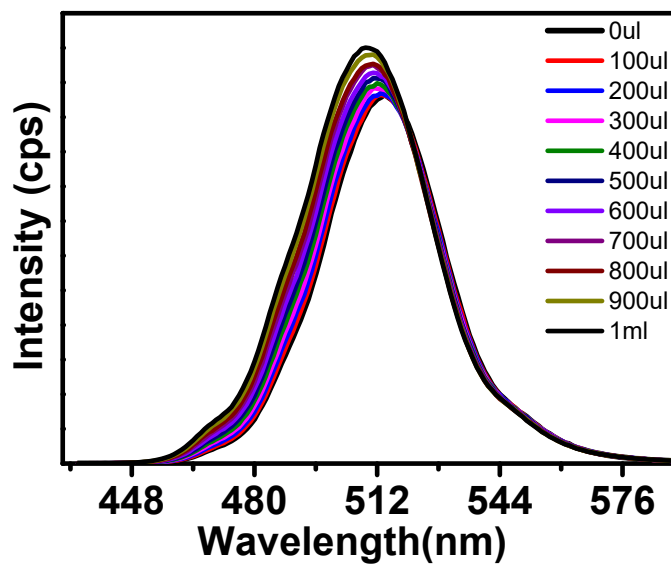


Fig. S9. The concentration dilution effect of P35 samples.

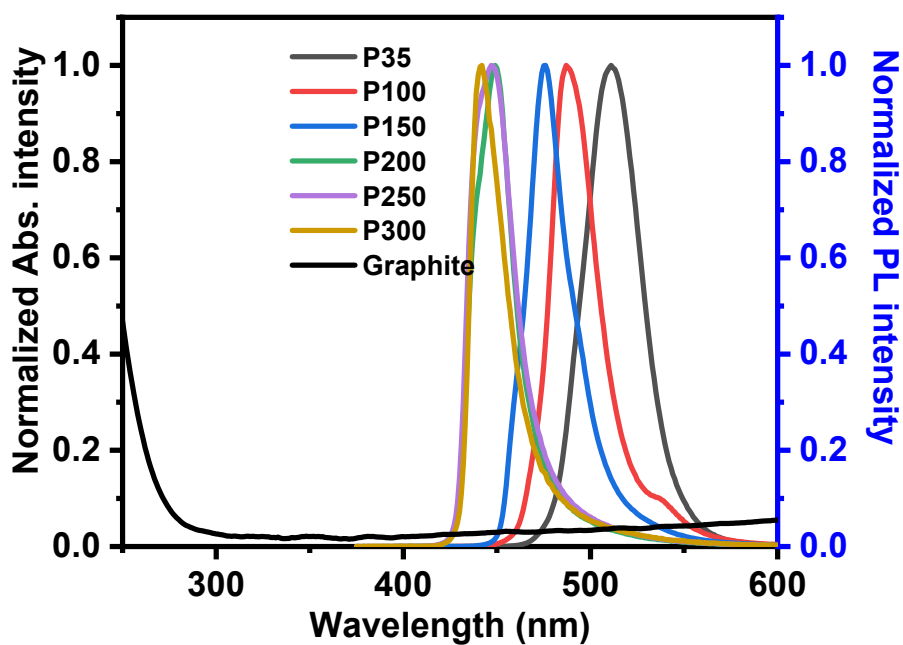


Fig. S10 Absorbance of graphite with emission of PNCs

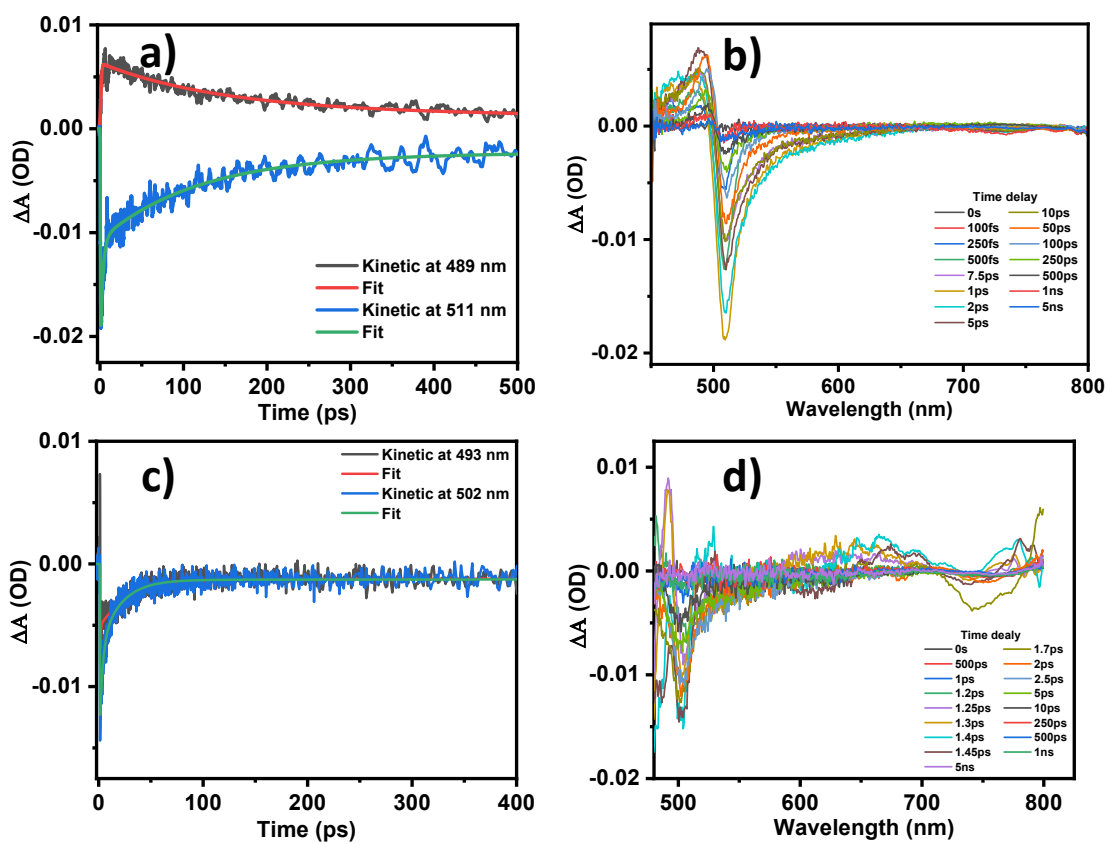


Fig. S11. TAS spectra of a) and b) for P300 and c) and d) for P300G.