Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Excitation Dependent Bidirectional Electron Transfer in Phthalocyanine-Functionalised MoS_2 Nanosheets

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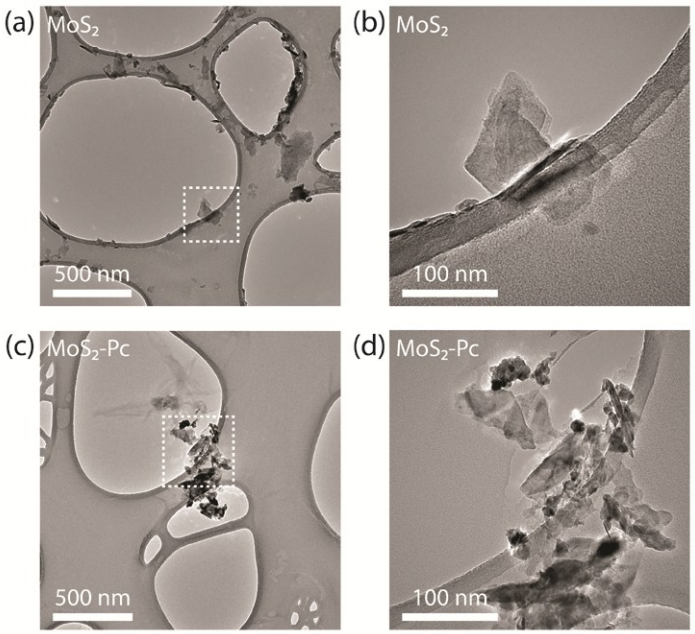

Figure S1: TEM images of the pristine MoS_2 (a) and PC functionalised MoS_2 (c). (b) and (d) show close up areas of the respective materials.

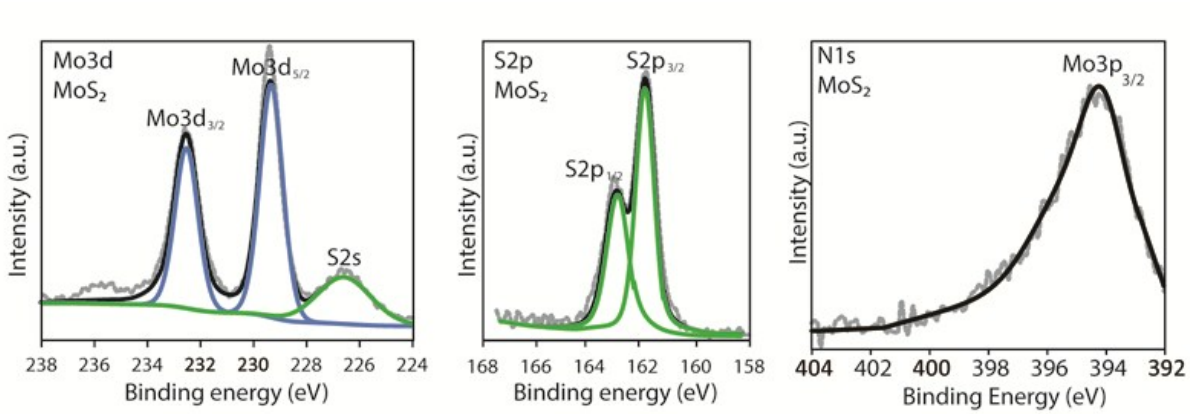

Figure S2: XPS of as exfoliated pristine 2D MoS_2 nanosheets

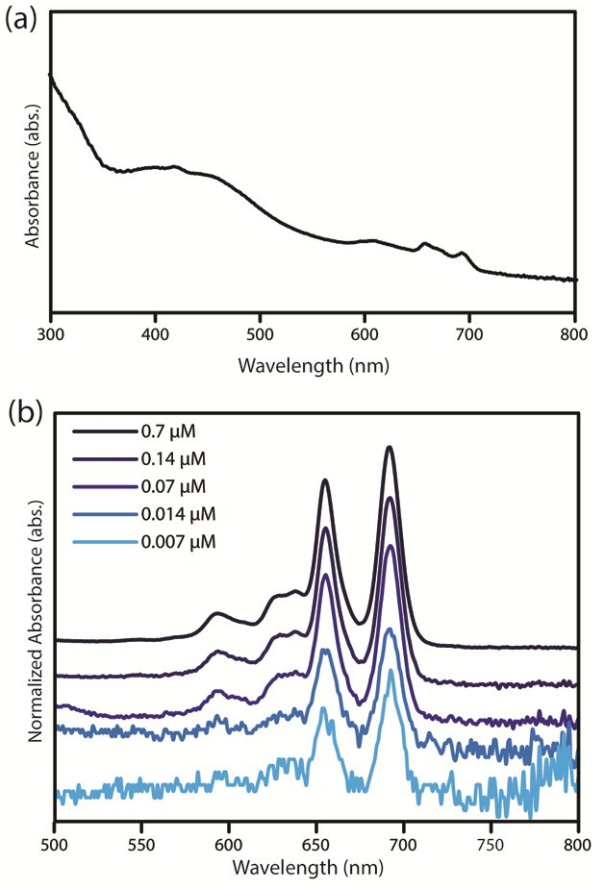

Figure S3: UV-vis spectra of the phthalocyanine functionalised MoS_2 (a) and multiple phthalocyanine concentrations (b) (normalised and off-set applied). The concentrations were determined using the Beer-Lambert Law and the extinction co-efficient as reported by Whalley.[1] The absorption peaks of the chromophore would be expected to shift with varying concentration if aggregation of phthalocyanine had occurred. The Q bands observed in b are in the same position as in the composite material (a) and Figure 3 in the main manuscript.

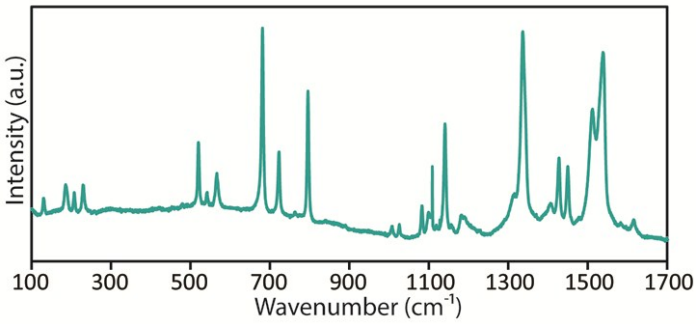

Figure S4: Raman spectroscopy of PC

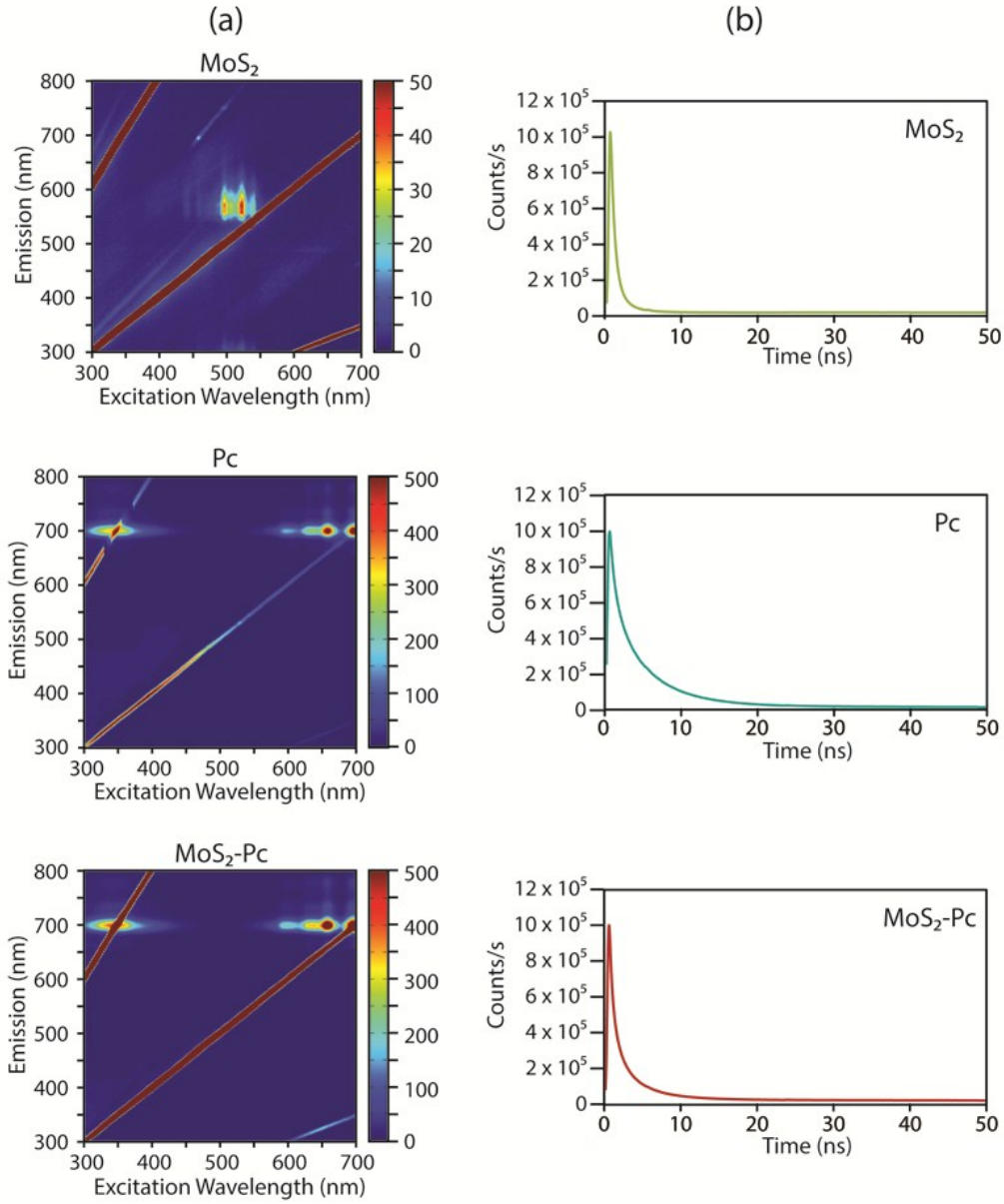

Figure S5: (a) Unfiltered PL Spectra and (b) PL decay curves of the respective materials excited at 510 nm. Decay lifetimes are determined to be 1.08 ns, 2.82 ns and 1.41 ns for pristine MoS_2, phthalocyanine and phthalocyanine functionalised MoS_2 respectively.

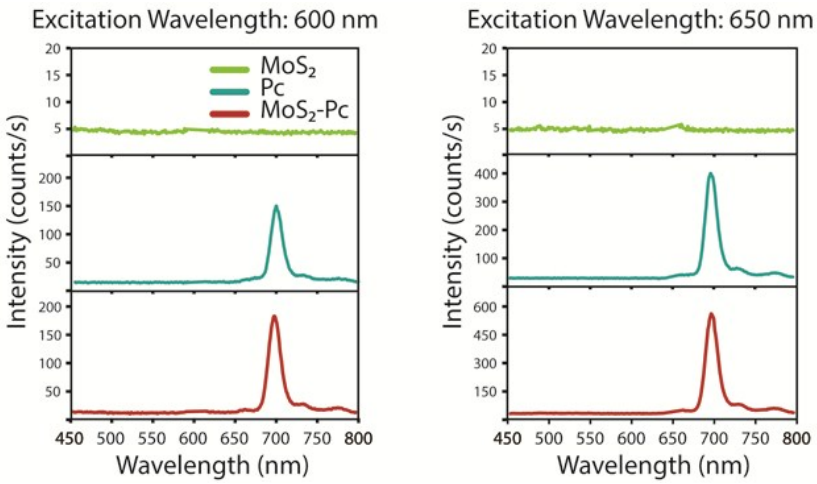

Figure S6: Individual PL spectra excited at 600 and 650 nm.

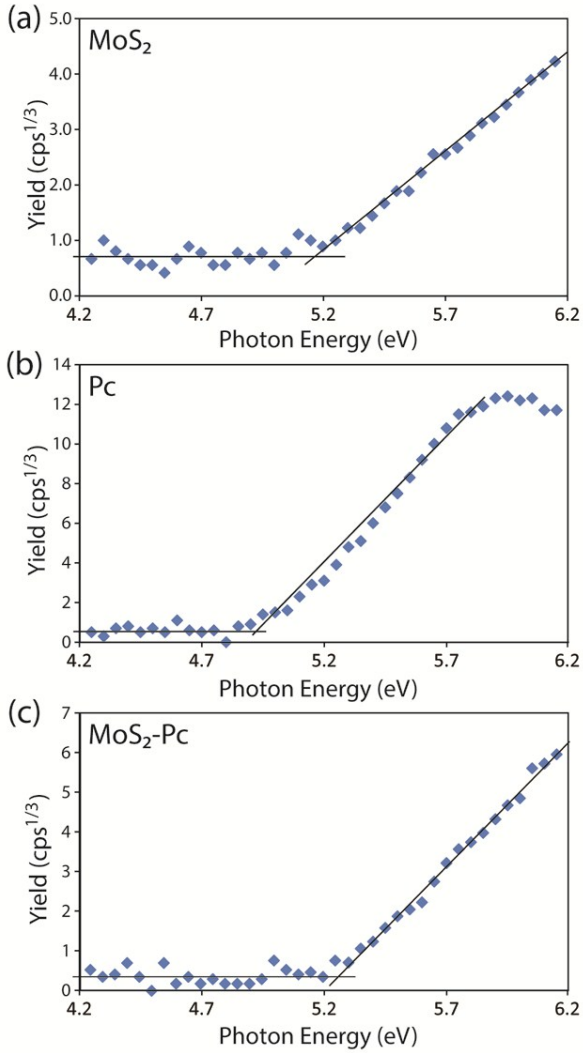

Figure S7: PESA measurements of the pristine MoS_2 (a), PC powder (b) and PC functionalised MoS_2 (c).

Calculation of the PL quantum yield:

The PL quantum yield of the composite material was calculated for the composite material. For this calculation the published quantum yield of phthalocyanine in toluene was used as a standard. The PL spectra shown in Figure S6 and the corresponding absorption spectra (not shown) were used for this calculation. The PL spectra were integrated to calculate the PL intensity $i_{PL(\lambda)}$ at a given excitation wavelength λ. The PL intensity was then corrected for variations of the absorption intensity $A_{(\lambda)}$ between the different samples at the corresponding excitation wavelength of λ giving the corrected PL intensity of $I_{PL(\lambda)}$ using equation 1.

$$I_{PL(\lambda)}=i_{PL(\lambda)}/A_{(\lambda)} \quad [1]$$

Using the literature value for the PL quantum yield (QY) of phthalocyanine in toluene being QY(Pc)= 0.67 we can calculate the QY of the composite at a given wavelength using equation 2.[2]

$$QY(MoS_2\text{-}Pc)= [I_{PL(\lambda)}(MoS_2\text{-}Pc)/ I_{PL(\lambda)}(Pc)]\times 0.67 \quad [2]$$

For an excitation wavelength of 650 nm we found a quantum yield of 18.7% for the phthalocyanine functionalised MoS_2 nanosheets, and 2.4% when an excitation wavelength of 600 nm is used. The lower yield observed in the second case is due to competitive absorption effects.

Transition	MoS_2	Pc-S1	Pc-S2
Pc	n/a	67%[3*]	0.10%[3*]
MoS_2	<0.3%[4*]	n/a	n/a
MoS_2-Pc	~0%[Γ]	18.70%[#]	~0% [Γ]

Table S1: Summary of observed and literature luminescence quantum yields for key transitions. [3*] and [4*] are values extracted from references 3 and 4 respectively, [Γ]spectral feature not observed, luminescence yield is close to 0% and [#] measured yield for excitation at the dye's Q_y band at 650 nm.

References

1. M. Whalley, *Journal of the Chemical Society (Resumed)*, 1961, DOI: 10.1039/JR9610000866, 866-869.
2. A. T. Gradyushko, A. N. Sevchenko, K. N. Solovyov and M. P. Tsvirko, *Photochem. Photobiol.*, 1970, **11**, 387-400.
3. D. Chahraoui, P. Valat and J. Kossanyi, *Res. Chem. Intermed.*, 1992, **17**, 219-232.
4. Z. X. Gan, L. Z. Liu, H. Y. Wu, Y. L. Hao, Y. Shan, X. L. Wu and P. K. Chu, *Appl. Phys. Lett.*, 2015, **106**, 233113.