# Electronic coupling and photoluminescence anisotropy in van-der-Waals-stacks of tungsten disulphide with molecular single crystals

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#### SUPPORTING INFORMATION

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#### 1. Crystal structure of PyMACl

The single crystal structure of PyMACl has been determined by the Sada group. <sup>1</sup> The compound crystallizes as colourless rectangular plates in the orthorhombic crystal system in the space group  $P2_12_12_1$  (no. 19). As shown in **Figure S1** (left), the pyrene moieties are arranged in slip-stack fashion. Each pyrene moiety has two equally close neighbours, as indicated by the centroid-to-centroid distances. This is in contrast pyrene, <sup>2</sup> where each molecule only has one closest neighbour, pre-arranging a dimer for excimer formation. The ionic interaction between methylammonium groups and chloride ions enforces an overall layer-like arrangement in PyMACl, with only van-der-Waals interactions between layers of pyrene moieties in the crystallographic *c*-direction. This specific packing allows for easy exfoliation and ensures that the heterostructure is created using the (001) crystal facet. In the optical experiments, the *ab*-plane of the exfoliated layers was facing upwards (**Figure S1**, right). The red arrow indicates the approximate orientation of the transition dipole moment in one molecular unit, assuming that the influence of the attached methylammonium group on the aromatic electron system is small.



Figure S1: Crystal structure of PyMACl in different orientations.





**Figure S2:** Optical setup for polarization resolved measurements. The polarization and the intensity of the laser source was controlled by a half wave plate combined with a linear polarizer. In the detection path, another linear polarizer was inserted to analyze the polarization of the luminescence emitted by the sample.

## 3. Tauc Plot of the PyMACl absorption edge



**Figure S3**: Tauc plot assuming a direct band edge and linear fits to determine the band edge energy. We estimate the absorption edge from the point where the fitted lines cross, corresponding to an energy of 3.19 eV.

#### 4. Intensity of the $X_A$ exciton inside and outside of the heterostructure

In order to explore different transfer mechanisms, it is instructive to examine the intensity of the tungsten disulphide ( $WS_2$ ) emission more carefully in regions of the heterostructure with PyMACl and outside of these regions. To compare the intensities, we use two independent approaches, one based on the recorded spectra and the other based on the PL images.

First, to compare the emission strength of the  $WS_2$  monolayer  $X_A$  exciton inside and outside of the heterostructure, the un-normalized spectra shown in **Figure 6.a,b** in the main text are compared to the un-normalized PL of neat  $WS_2$ , see **Figure S3a**. After correcting the spectral data for the excitation power and the settings for integration time and averaging used during their acquisition, both signatures are approximately similar in emission strength. The  $WS_2$  peak from the neat monolayer is slightly enhanced compared to the  $WS_2$  emission in the heterostructure, as estimated from the difference spectrum. This is actually expected if there is a hole transfer from the predominantly excited  $WS_2$  to PyMAC1.



**Figure S4**: Comparison of  $WS_2$  (neat layer) emission with the HS and PyMACl (a) and with the difference spectra (b). PL are corrected for the employed excitation densities.

Second, a more direct comparison of the PL intensities is performed by checking the intensity of the PL images recorded with the microscope. Therefore, we analyse the intensity of the red colour channel of the RGB fluorescence images that were recorded under homogeneous excitation of a spatially widened 400 nm diode laser source, as shown in **Figure S4**. The intensity is plotted along the profile lines drawn in the monochrome (red) images. For both the heterostructure with PyMACl on top of WS<sub>2</sub> and for the inverted heterostructure, we find that the overall intensity of the WS<sub>2</sub> emission outside of the heterostructure region is brighter, as indicated by the number of counts extracted from certain regions of the images. The results support the view that the WS<sub>2</sub> emission is partially quenched by the organic PyMACl layer, potentially through a hole transfer.



**Figure S5**: Analysis of the WS<sub>2</sub> emission intensity inside the heterostructure (HS) region and outside. Panels (ab) show the PL images of the HS and the inverted HS, respectively. PyMACl emits yellow PL, whereas the WS<sub>2</sub> monolayer appears red. The RGB images were split into their individual colour channels and further analysed using *ImageJ*. The images given by the red channel, where the emission of WS<sub>2</sub> dominates, are presented in (d-e). The intensities along the yellow profile lines are plotted in (f-h). Even though quantitative statements are not possible due to saturation of the intensity and overlapping PyMACl and WS<sub>2</sub> emission, we find that the overall WS<sub>2</sub> emission inside the HS fainter compared to the region outside of the HS.

#### 5. Relative photoluminescence intensities

**Figure S6** below shows the time-integrated PL intensities obtained for the two spectral ranges that were assigned to free exciton and excimer emission. Overall, the data reproduces the trends that were also observed for the PL lifetimes, thereby supporting the assumption that non-radiative processes such as recombination or charge- and exciton-transfer at the heterointerface are responsible for the observed PL dynamics. It should be noted that a systematic error in our displayed intensities occurs, because the time scale of the decay exceeds the time window of the measurement. However, this should not affect the generally observed trends, i.e. the free exciton emission decreases upon heating, whereas we find a slight increase for the excimer emission.



**Figure S6**: Time-integrated PL-intensities. In the temperature dependent time-integrated spectra of PyMACl (a) and the HS (b), the spectral regions of free exciton and excimer emission are highlighted by different colors (free exciton: blue, excimer: red). The intensities integrated over these spectral ranges are presented in (d-e).

#### 6. Inverted WS<sub>2</sub>-PyMACl heterostructure (HS)

In order to rule out a filtering effect as the cause for the observed polarized emission emerging from  $WS_2$ , an inverted HS with  $WS_2$  on top of PyMACl was fabricated and studied analogously. Comparing **Figure S7** and **Figure 6** in the main text, similarities and differences are observable. Compared to the difference spectra in **Figure 6**, the red-shifted emission (RSE) in **Figure S7** seems much broader and more intense and it overlaps with the  $X_A$  signature, giving rather the impression of a single feature. However, investigating the  $X_A$  and RSE spectral regions, as established for **Figure 6**, we find that the feature consists of at least two different signatures, revealed by the differing orientation in their polarization, see **Figure S7.f**. Similar to the HS introduced in the main text, we observe a change of the  $X_A$  polarization from isotropic (**Figure S7.e**) to linear when  $WS_2$  is stacked with the organic compound (**Figure S7.f**), which is shifted by roughly 90° with respect to the yellow PyMACl emission. Differing from the case presented in **Figure 6.f**, the  $X_A$  and the RSE signature in **Figure S7.f** are not oriented in the same direction, but shifted by 40-60° with respect to each other.



**Figure S7**: Polarization resolved characterization of the inverted  $WS_2$ -PyMACl HS. In order to extract the intensity of the  $WS_2$  exciton emission ( $X_A$ ), the PL background of PyMACl was recorded outside the HS region, normalized to the PL spectrum of the HS in the energy range between 2.10 and 2.12 eV (a) and subtracted from the HS data, yielding the difference spectrum presented in (b). Polarization dependent emission spectra and difference spectra are presented as false-colour plots in (c) and (d). Polar plots of the integrated intensities of PyMACl, the  $X_A$  peak (neat WS<sub>2</sub> and HS) and the RSE peak are shown in panels (e) and (f).

#### 7. PyMACI: Exciton and excimer polarization

The detection range for the polarization resolved measurements after preferential excitation of WS<sub>2</sub> was limited to lower emission energies and did not allow us to extract information about the polarization of the free exciton emission. In order to complete the picture regarding the polarization of the different emissive species present in the PyMACl/WS<sub>2</sub> HS, we also carried out static PL measurements in a range of higher emission energies. In order to improve the luminescence yield, the sample was placed in a cryostat (CryoVac) and cooled down to 80 K via liquid nitrogen flow. A PyMACl crystal was excited at 370 nm via a frequency doubled titanium-sapphire laser pulse. The emitted PL was then separated from the reflected laser radiation with a 376 nm dichroic long pass filter, after which the spectrum was recorded by a monochromator coupled to an EMCCD camera (Andor iXon Ultra). By placing a polarizer into the detection path, which was turned by 10° between each measurement, the polarization dependence of the PL signatures and the orientations of their respective polarizations could be investigated. Surprisingly, the static PL spectrum seen in Figure S8.a revealed two additional broad peaks between the expected free exciton signal at 2.9 eV and the excimer emission between 1.9 to 2.4 eV, which were not observed in the TRPL measurements displayed in Figure 2.c. These additional peaks might result from the emission of longer-lived species, which only start to dominate the spectrum after the 2 ns time window, or the different spectra could originate from the different excitation conditions employed in different setups. The polarization series reveals a distinct difference in polarization orientation between the observed signatures. Although the polarization of the signatures is on the weaker side, a clear preferential direction can be observed for the excimer signal, see Figure S8.c, similar to the previously measured ellipsoid shape presented in Figure 6.e in the main text. The higher energy peaks including the free exciton signature exhibit a lesser degree of polarization which is shifted by roughly 45° with respect to the polarization of the excimer emission, giving clear evidence for its different origin, i.e. the free exciton state.



**Figure S8:** Static PL measurement polarization series on PyMACl single crystal at 80 K. The investigation focuses on the spectral region of the free exciton (2.88-3.18 eV) highlighted in blue, and the yellow excimer emission (1.81-2.34 eV), highlighted in red. In (a) the spectra at which each species shows it maximum emission are shown. Panel (b) displays a false colour plot of the polarization dependent emission spectra. A polar plot with the integrated intensity over the mentioned spectral regions is presented in (c).

### 8. Literature

1 N. Tokunaga, Y. Fujiki, S. Shinkai and K. Sada, Chem. Commun., 2006, 2, 3617–3618.

2 A. Camerman and J. Trotter, Acta Crystallogr., 1965, 18, 636–643.