

Electronic Supplementary Information

**Organic phototransistors based on perylene diimide nanocrystals
lacking π – π interactions.**

Ilya Bronshtein,^a Mark A. Iron,^b and Boris Rybtchinski^a

^aDepartment of Organic Chemistry, Weizmann Institute of Science, Rehovot 7610001, Israel.

^bComputational Chemistry Unit, Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 7610001, Israel.

*Correspondence to: boris.rybtchinski@weizmann.ac.il

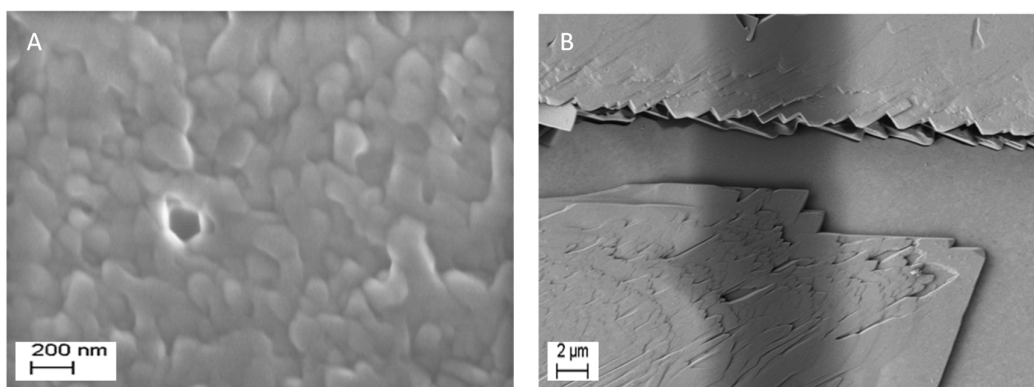


Figure S1. (A) Thin film of PVD-evaporated DMP-PDI crystals on HMDS-treated substrate. (B) Thin film of unsonicated DMP-PDI crystals deposited by a LB process.

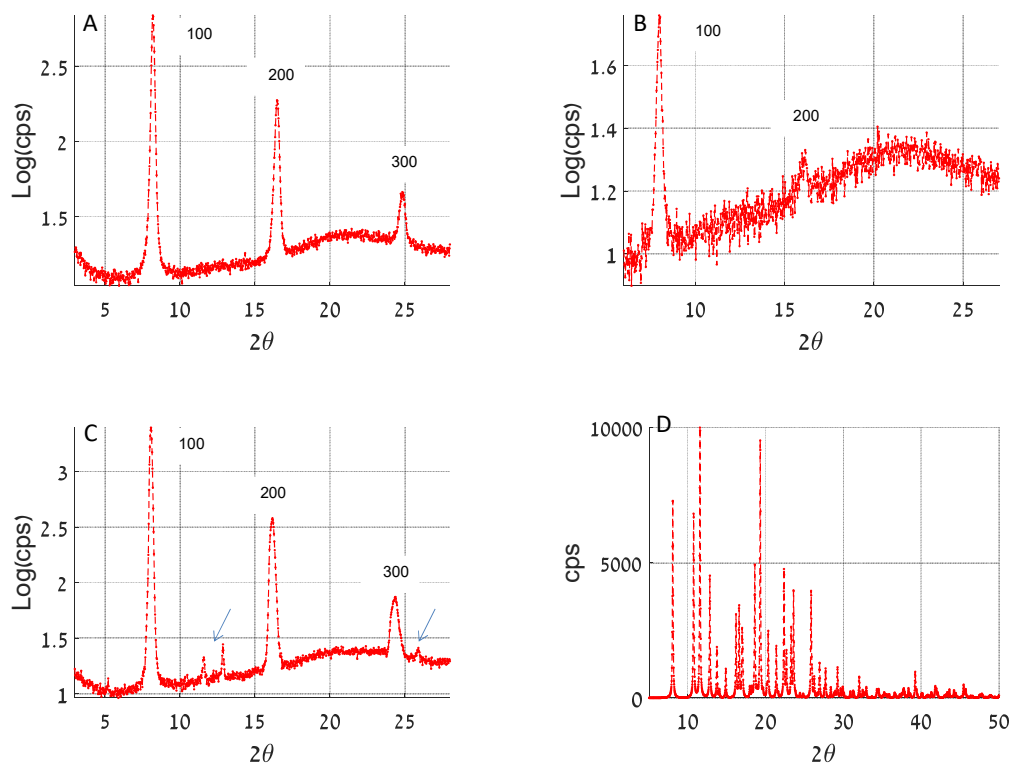


Figure S2. Powder X-ray diffractograms of DMP-PDI nanocrystalline films: (A) nanocrystals deposited on a silicon substrate surface from a sonicated solution. (B) PVD-deposited DMP-PDI on a silicon substrate. (C) Nanocrystals deposited from an unsonicated solution. (D) Simulated diffractogram of a single crystal using Mercury software.^{S1}

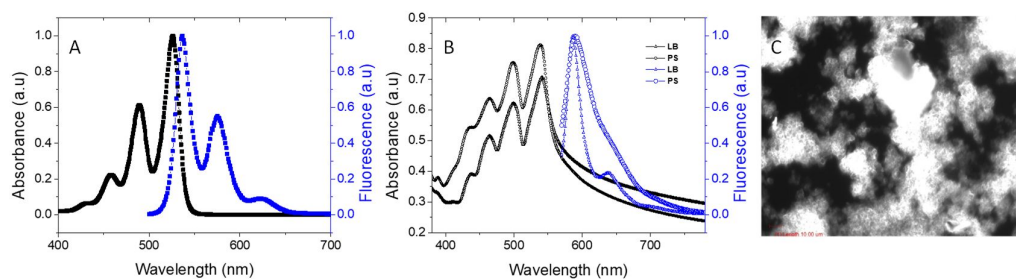


Figure S3. (A) UV-vis (black) and fluorescence (blue) spectra of a 10^{-4} M DMP-PDI solution in chloroform. (B) UV-vis (black) and fluorescence (blue) spectra of DMP-PDI nanocrystals assembled in solution (LB process, triangles) and the PS/DMP-PDI hybrid film (PS, circles). (C) Fluorescence microscopy image of the of DMP-PDI nanocrystals deposited from solution.

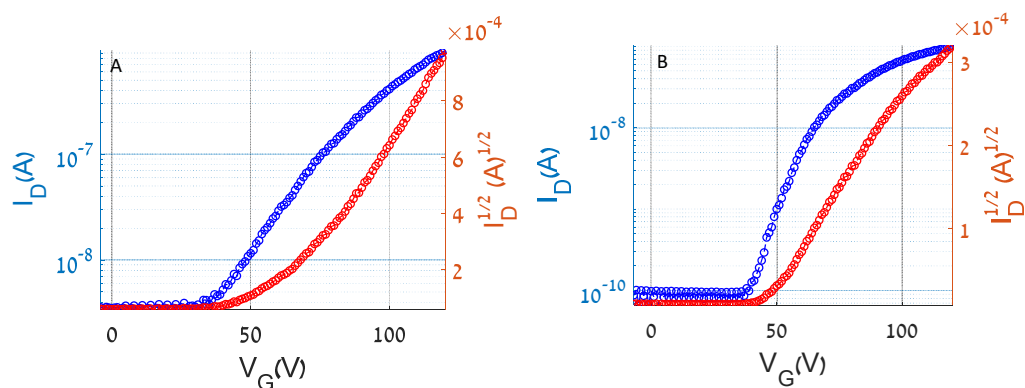


Figure S4. Transfer characteristics of bottom-contact bottom-gate OPTs based on DMP-PDI films deposited on substrate treated with spin-coated HMDS. (A) Nanocrystals deposited from solution on a silicon substrate. (B) PVD-deposited crystals.

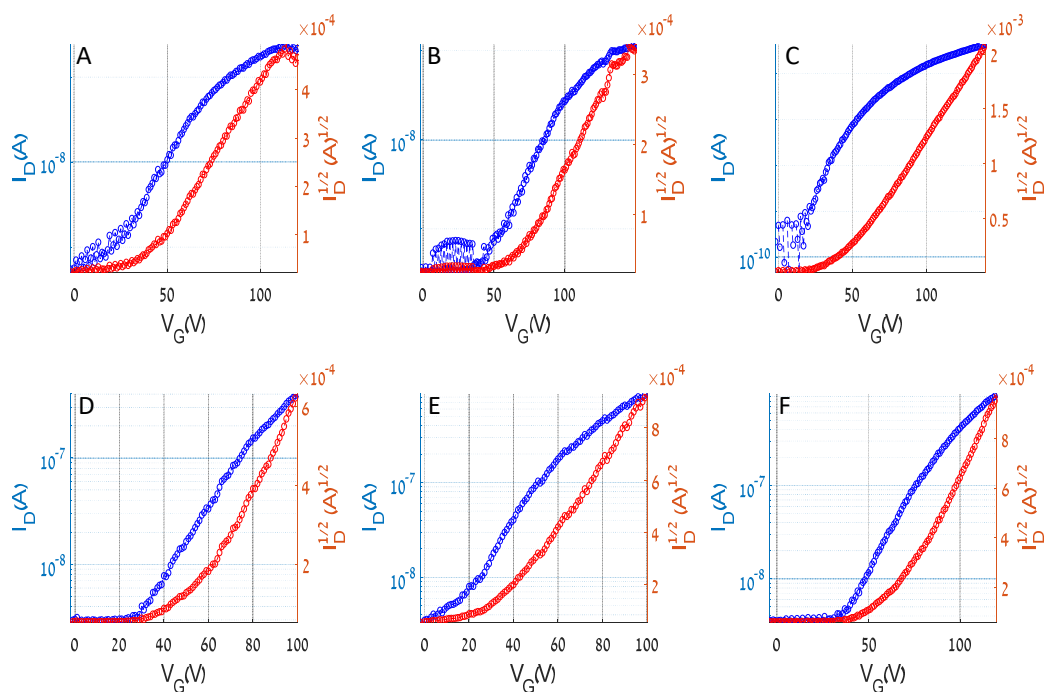


Figure S5. Transfer characteristics of bottom-gate bottom-contact OFETs based on DMP-PDI films: untreated substrate under illumination (A) and in the dark (B), substrate treated with spin-coated HMDS under illumination (C) and in the dark (D); substrate treated with by vapor deposited HMDS under illumination (E) and in the dark (F).

Table S1. Influence of HMDS treatment.

	Substrate treatment	Illumination	Mobility $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	V_{th} (V)
A	No	No	0.0001	57
B	No	Yes	0.0002	34
C	HMDS spin-coating	No	0.0004	55
D	HMDS spin-coating	Yes	0.0007	35
E	HMDS vapor deposition	No	0.0002	51
F	HMDS vapor deposition	Yes	0.0003	28

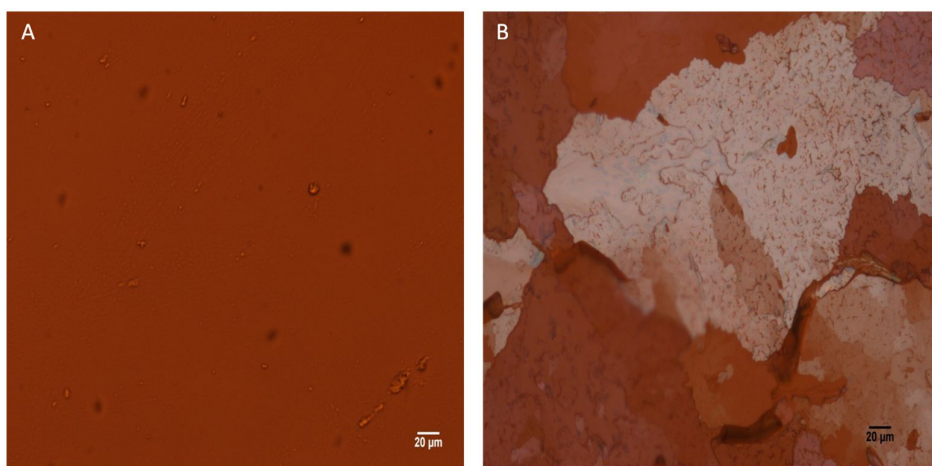


Figure S6. Cross-polarized optical microscopy images of DMP-PDI/PS hybrid thin film: (A) pristine blend and (B) annealed at 210 °C for 10 min.

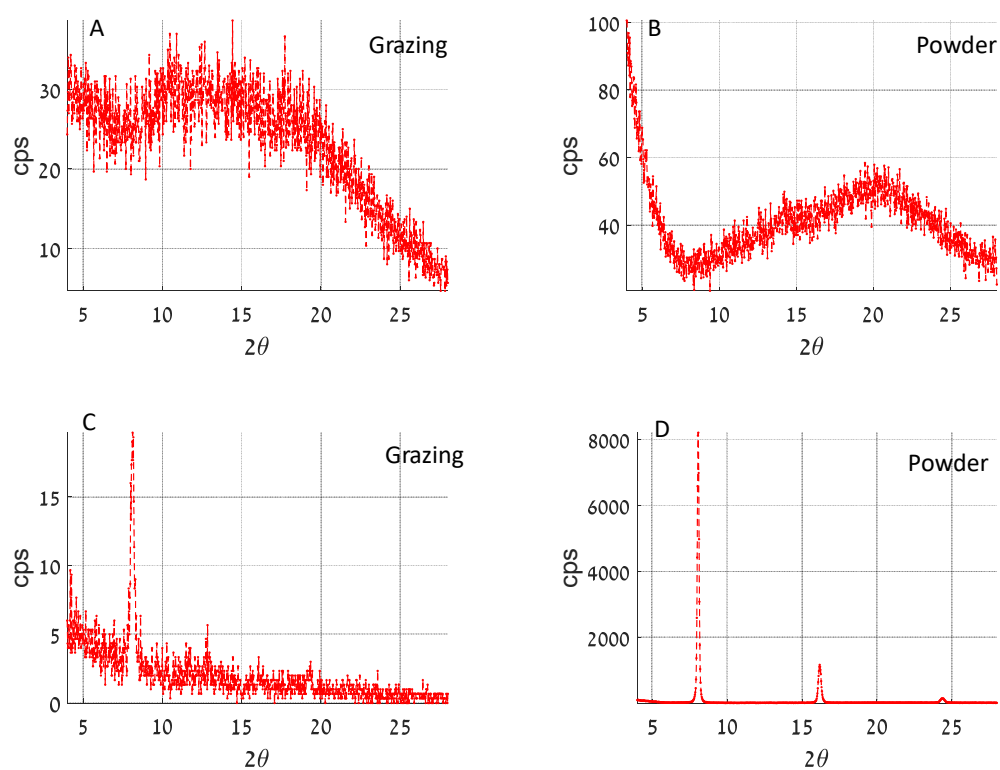


Figure S7. Powder and grazing X-ray diffractograms of DMP-PDI/PS hybrids before (A,B) and after (C,D) annealing at 210 °C for 10 min.

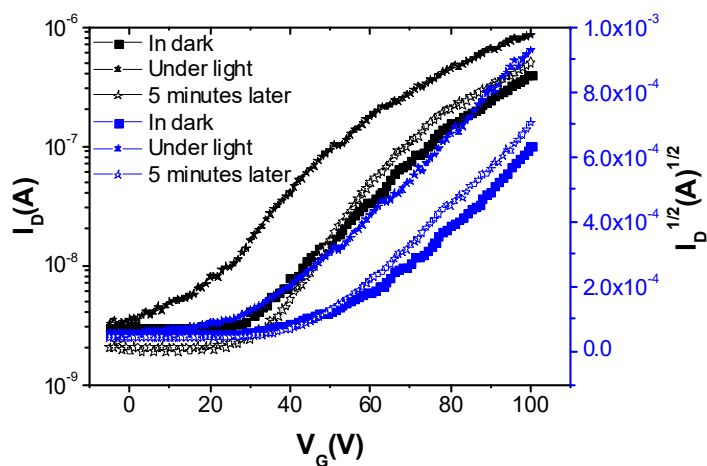


Figure S8. Transfer characteristics of OPTs based on DMP-PDI films deposited from solution (by LB, on HMDS-spin coated silicon substrate): before, during and 5 min after illumination.

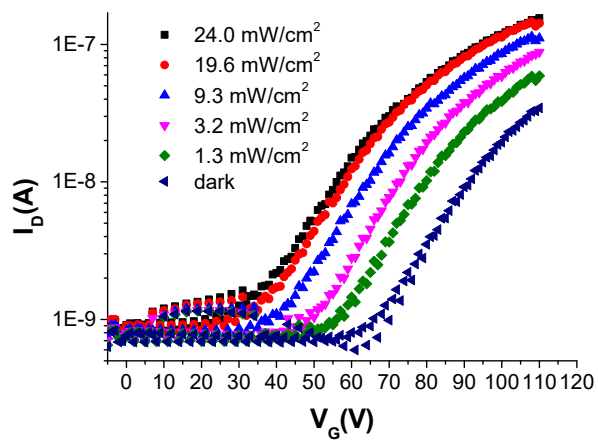


Figure S9: Transfer characteristics of OPTs based on DMP-PDI films deposited on a HMDS-treated silicon substrate measured in the dark or under illumination with white light with various light intensities at $V_D=120$ V.

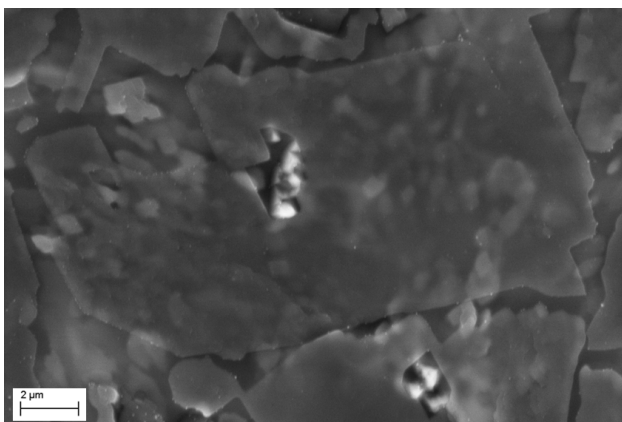


Figure S10. SEM image of the DMP-PDI/PS hybrid film.

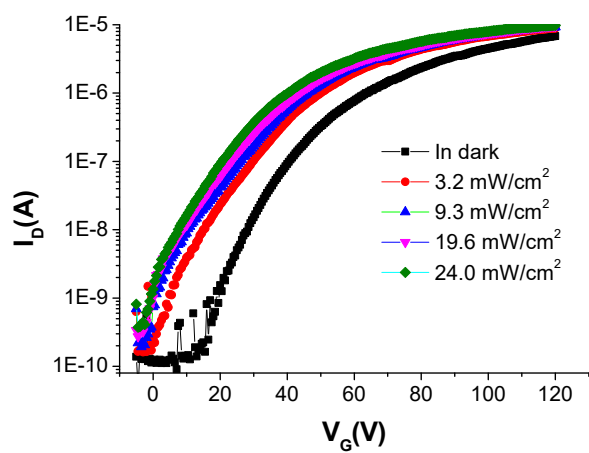


Figure S11 : Transfer characteristics of the of OPTs based on DMP-PDI/PS hybrid films measured in the dark or under illumination with white light with various light intensities at $V_D=120$ V.

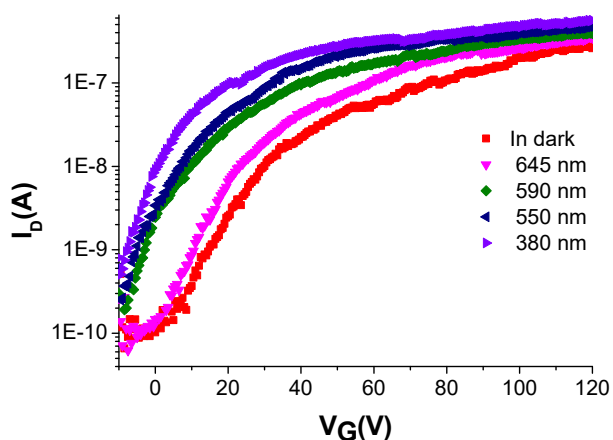


Figure S12: Transfer characteristics of the of OPTs based on DMP-PDI/PS hybrid films under white light illumination of 24 mW/cm^2 at $V_D=120 \text{ V}$, with color cut filters of 645, 590, 550, 500, 380 nm and in dark.

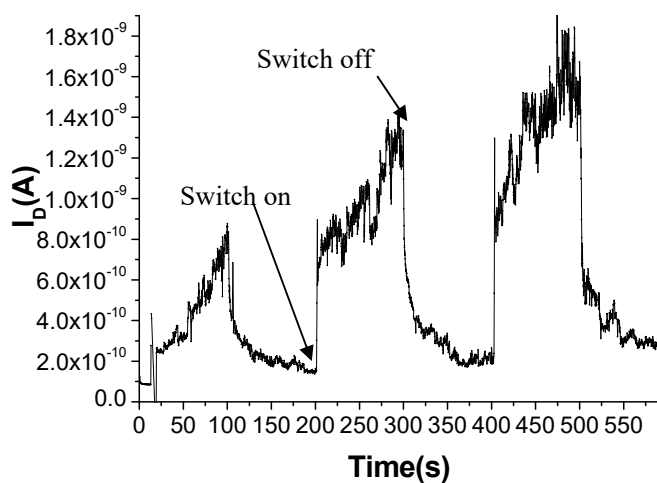


Figure S13: Photocurrent characteristics of OPTs based on DMP-PDI/PS hybrid films under white light illumination of 24 mW/cm^2 at $V_G=0\text{V}$ and $V_D=120\text{V}$. The light was switched on and off manually during the measurement.

The upward slope of the photocurrent upon light irradiation and the downward slope under turning off the light condition could be related to charge accumulation and release rates.²

Table S2. Components of the sSAPT(0)/jun-cc-pVDZ calculation (in kcal/mol) and Hobza's ratio (unitless) for DMP-PDI.

electrostatics	-8.94
exchange	22.37
induction	-2.69
dispersion	-26.90
total	-16.16
total/n	0.54
R _{Hobza}	3.01

R_{Hobza} value: As proposed by Řezáč *et al.*,^{S3} the dispersion versus electrostatic nature of a complex is considered based on the ratio $R_{\text{Hobza}} = E_{\text{dispersion}}/E_{\text{electrostatics}}$ of the dispersion and electrostatic energetic components of a SAPT calculations: values greater than 1.70 are “dispersion-bound,” values less than 0.59 are “electrostatically bound” while intermediate values are “mixed influence. The ratio of 3.01 obtained here for DMP-PDI indicates that the interaction is strongly dispersion-bound.

- 1 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. Van De Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453–457.
- 2 H. Yu, Z. Bao and J. H. Oh, *Adv. Funct. Mater.*, 2013, **23**, 629–639.
- 3 J. Řezáč, K. E. Riley and P. Hobza, *J. Chem. Theory Comput.*, 2011, **7**, 2427–2438.