Electronic Supplementary Information

2,2'-(Arylenedivinylene)bis-8-hydroxyquinolines exhibiting aromatic π-π stacking interactions as solution-processable p-type organic semiconductors for high-performance organic field effect transistors

Suman Sehlangia,[a] Shivani Sharma,[b] Satinder K. Sharma,*[b] Chullikkattil P. Pradeep*[a]

[a] School of Basic Sciences, Indian Institute of Technology Mandi, Kamand-175 005, Himachal Pradesh, India. Fax: +91 1905 267009; Tel: +91 1905 267045; E-mail: pradeep@iitmandi.ac.in
[b] School of Computing and Electrical Engineering, Indian Institute of Technology Mandi, Kamand-175 005, Himachal Pradesh, India. Fax: +91 1905 267009; Tel: +91 1905 267134; E-mail: satinder@iitmandi.ac.in

Table S1. Crystal and structure refinement data of D1

Empirical formula	$C_{29}H_{24}N_2O_4S$
Formula weight	496.56
Crystal system	monoclinic
Space group	$P2_{1/c}$
a	18.015(2) Å
b	4.7644(5) Å
c	28.334(5) Å
α	90.00°
β	107.959(16)°
γ	90.00°
V	2313.4(6) $Å^3$
Z	4
ρ	1.426 g/cm^3
μ	1.583 mm^{-1}
F (000)	1040.0
T	150.0(5) K
Reflections collected	3115
Independent reflections	2375 [R_{int} = 0.0669, R_{sigma} = 0.0698]
Data/ restraints/parameters	2375/0/332
Final R indices [I>=2σ(I)]	R_1 = 0.0861, wR_2 = 0.1940
R indices (all data)	R_1 = 0.1009, wR_2 = 0.2060
GOF	1.037

Crystallographic Alerts (A and B level) from CheckCIF and the author responses:

1) PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.608 Why?

   Author response: incomplete coverage of diffraction patterns and some data were rejected as poor during integration and scaling.

2) PLAT201_ALERT_2_A Isotropic non-H Atoms in Main Residue(s) ..... 16 Report

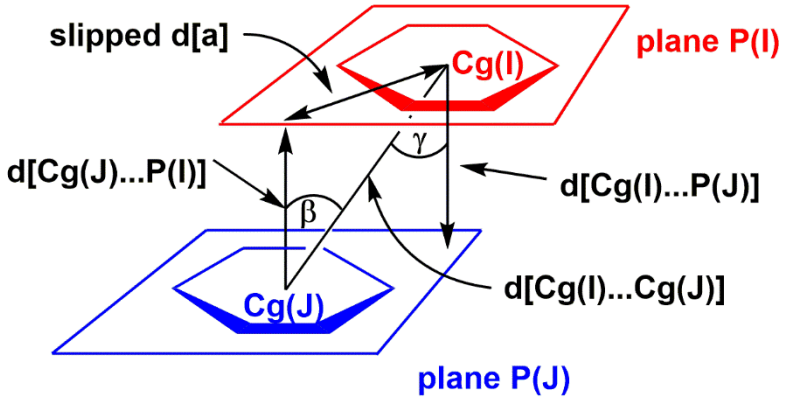
   Author response: Lack of data quality due to poorly diffracting nature of the crystals.

3) PLAT911_ALERT_3_B Missing FCF Refl Between Thmin & STh/L= 0.597 1612 Report

   Author response: incomplete coverage of diffraction patterns and some data were rejected as poor during integration and scaling. Some reflections may have been stopped by the beam stop.

Analysis of supramolecular π-stacking interaction in the crystal structure of D1

The 'Analysis of short ring interactions' obtained using the CALC ALL option of PLATON[1,2] were used. Out of the several such interactions listed, only the strong interactions characterized by short centroid-centroid contacts (< 3.8 Å), near parallel ring planes (α < 10° to ~0°), small slip angles (β, γ < 25°) and vertical displacements (slippage < 1.5 Å), which denote sizable overlap of the aryl plane areas, were considered.[3,4] These interactions are listed in Table S2 below.



Scheme S1. Graphical presentation of the parameters used for the description of π-π stacking interactions.

- Cg(I) = Ring Center-of-Gravity (Plane number I)
- α = Dihedral angle between planes I and J (°)
- β = Angle Cg(I)-->Cg(J) vector and normal to plane I (°)
- γ = Angle Cg(I)-->Cg(J) vector and normal to plane J (°)
- d[Cg(I)···Cg(J)] = Distance between ring centroids (Å)
- d[Cg(I)···P(J)] = Perpendicular distance of Cg(I) on ring J (Å)
- d[Cg(J)···P(I)] = Perpendicular distance of Cg(J) on ring I (Å)
- Slippage d[a] = Distance between Cg(I) and perpendicular projection of Cg(J) on ring I (Å).

Table S2: Packing analyses for possible π-π interactions in D1 (see Scheme S1 above for details)

Cg(I)	Cg(J)	[ARU(J)]	d[Cg-Cg] (Å)	α (o)	β (o)	γ (o)	d[Cg(I)···P(J)] Å	d[Cg(J)···P(I)] Å	Slippage d[a] (Å)
Cg(1)	Cg(4)	1565.01	3.725	1.7	20.4	18.8	3.5262	3.491	1.298
Cg(2)	Cg(5)	1545.01	3.720	1.77	19.1	19.6	3.5050	3.5156	1.215
Cg(4)	Cg(1)	1545.01	3.724	1.7	18.8	20.4	3.491	3.5260	1.199
Cg(5)	Cg(2)	1565.01	3.720	1.77	19.6	19.1	3.5156	3.5052	1.246

[1565] = x, 1+y, z; [1545] = x, -1+y, z.

The Cg(I) refers to the Ring Center-of-Gravity numbers given in ( ) as follows: Cg(1) = Ring N1-C10-C11-C12-C13-C18; Cg(2) = Ring N2-C21-C22-C23-C24-C29; Cg(4) = Ring C13-C14-C15-C16-C17-C18; Cg(5) = Ring C24-C25-C26-C27-C28-C29.

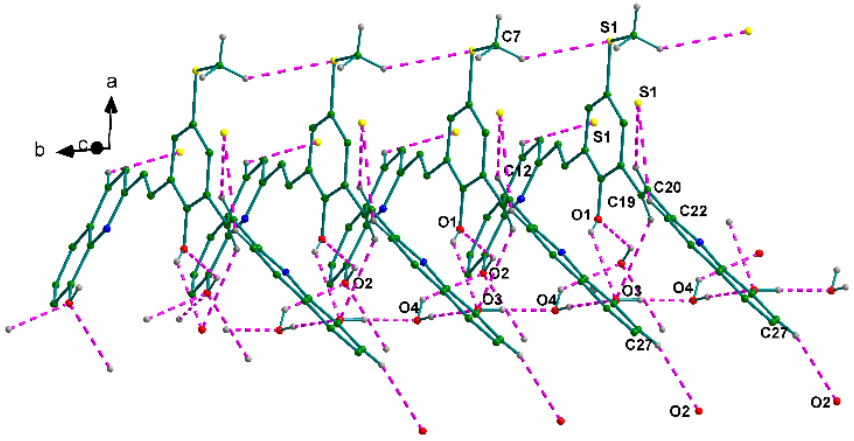


Figure S1. Various H-bonding and other weak-bonding interactions supporting the π-π stacked 1-D chain-like arrangements in the crystal lattice of **D1**.

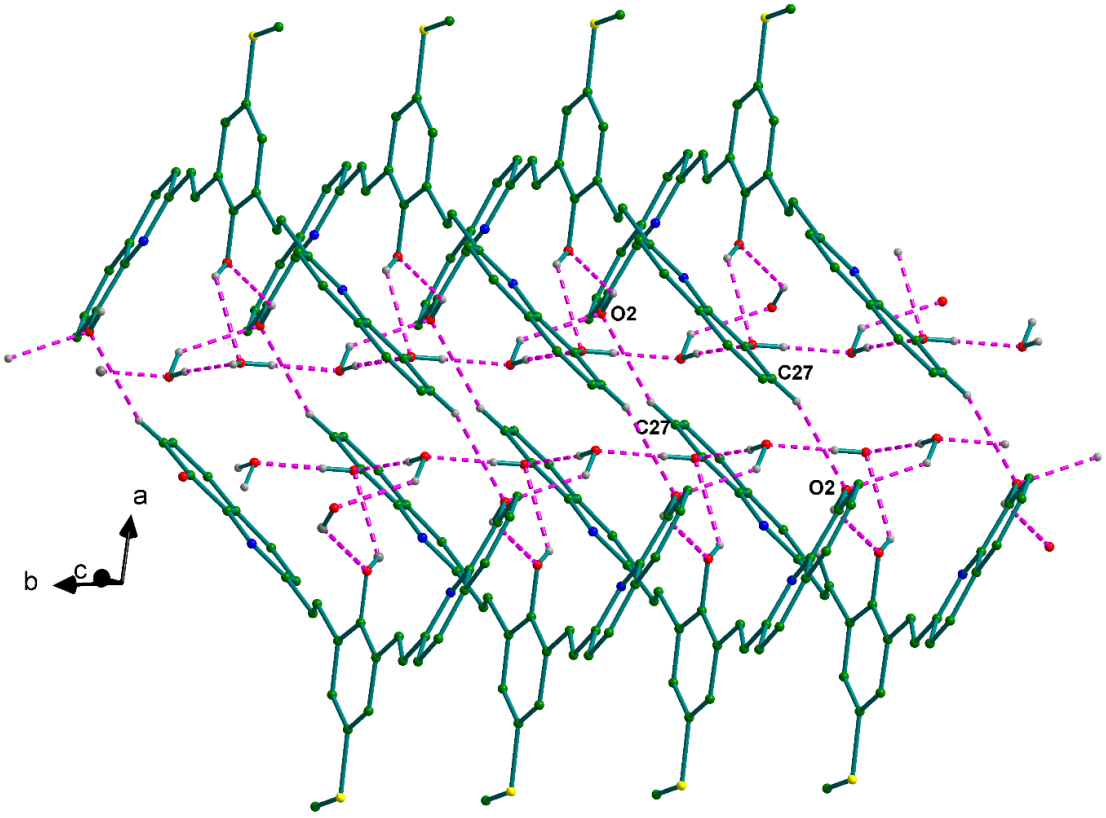


Figure S2. The inter-connection of adjacent 1-D chain-like structures through C–H···O interactions in a centro-symmetric fashion in the crystal lattice of **D1**.

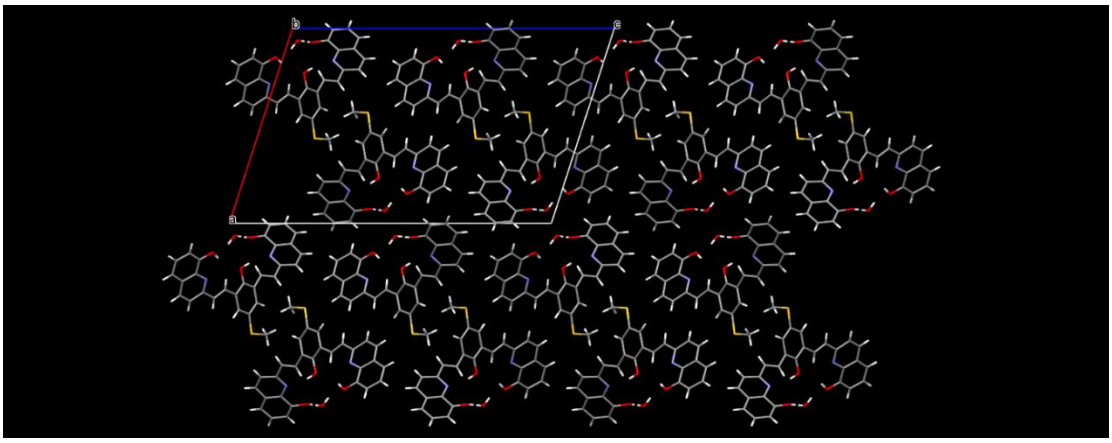


Figure S3. The overall packing arrangement of 1-D chain-like structures in the crystal lattice of **D1** as viewed along crystallographic *a* axis.

Cyclic Voltammetric Analyses of D1 and D2

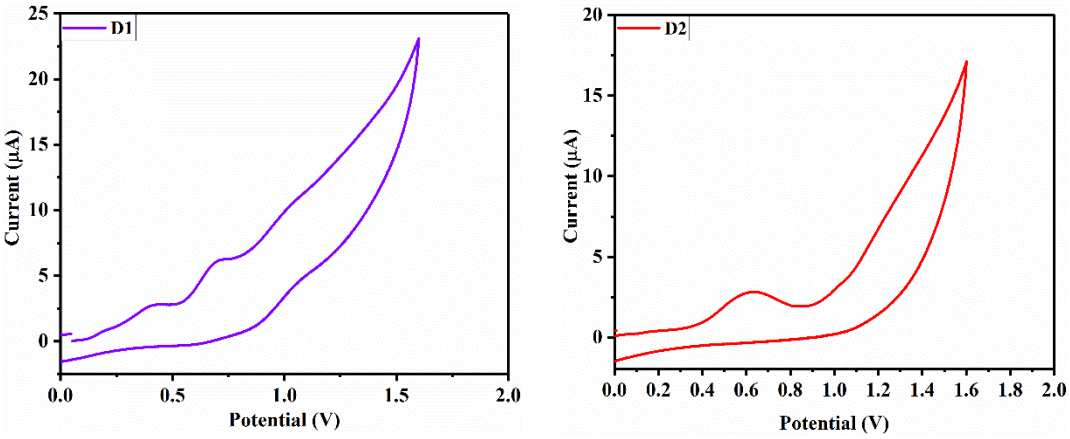


Figure S4. Cyclic voltammograms of **D1** (1.0 mM) and **D2** (1.0 mM) in DMF solutions at a scan rate of 50 $mV \cdot s^{-1}$, with Pt as the working and counter electrodes, Ag/AgCl electrode as the reference electrode, and n-Bu_4NPF_6 (0.1 M) as the supporting electrolyte.

TGA curves of D1 and D2

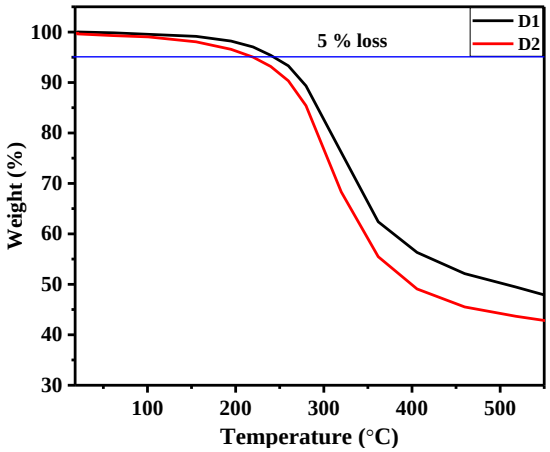


Figure S5. TGA curves of **D1** and **D2**.

DFT simulation of D1 and D2

The HOMO and the LUMO energy levels of **D1** and **D2** were simulated at the B3LYP/6-31G(d) level by Gaussian 09[5] and the results are presented in Table 2 (Main text) and Figure S6, below. These calculations confirm that the LUMOs of **D1** and **D2** are mainly localized on one of the 8-HQ groups while the HOMOs are localized on the other 8-HQ moiety.

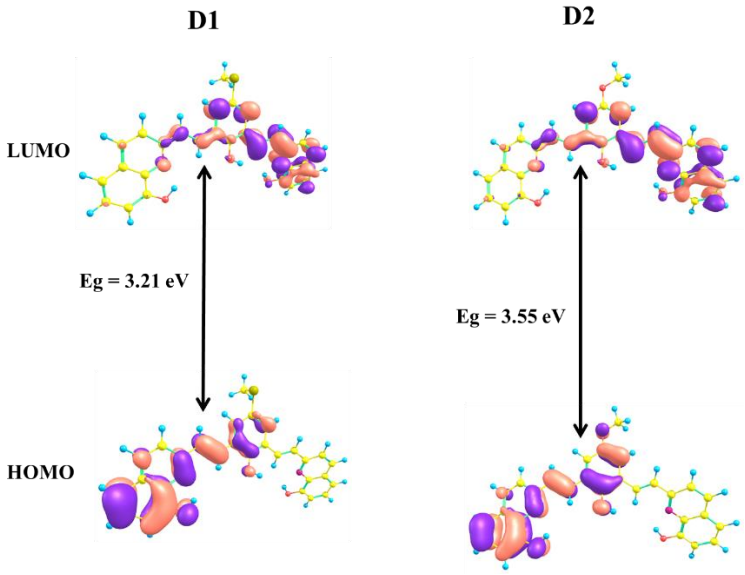


Figure S6. HOMO–LUMO diagrams and energy band gap of geometrically optimized **D1** and **D2**.

Output and transfer characteristics of OTFTs with thin films

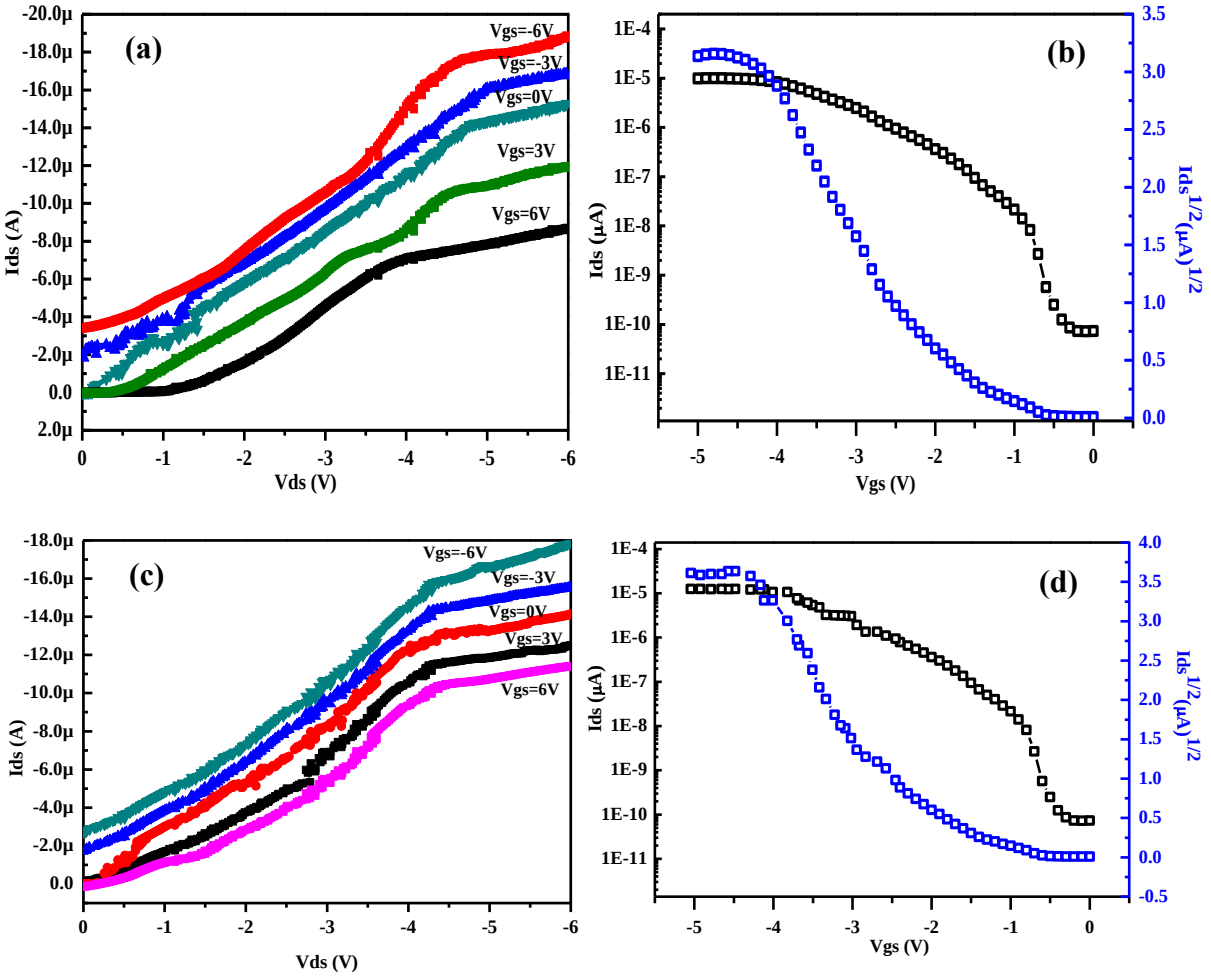


Figure S7. Electrical characteristics of the Ag/**D1**/PMMA/ITO on Glass substrate at 25°C and 50°C; (a) output characteristics of Ag/**D1**/PMMA/ITO at 25°C, where V_{ds} was swept from 0 to –6 V at V_{gs} varied from 6 to –6 V with the step of 3 V; (b) I_{ds} vs V_{gs} (logarithmic and linear scale) at V_{ds} = –6 V for gate voltage varying from –5 V to 0 V for Ag/**D1**/PMMA/ITO at 25 °C; (c) output characteristics of Ag/**D1**/PMMA/ITO at 50 °C, where V_{ds} was swept from 0 to –6 V at V_{gs} varied from 6 to –6 V with the step of 3 V; (d) I_{ds} vs V_{gs} (logarithmic and linear scale) at V_{ds} = –6 V for gate voltage varying from –5 V to 0 V for Ag/**D1**/PMMA/ITO at 50 °C.

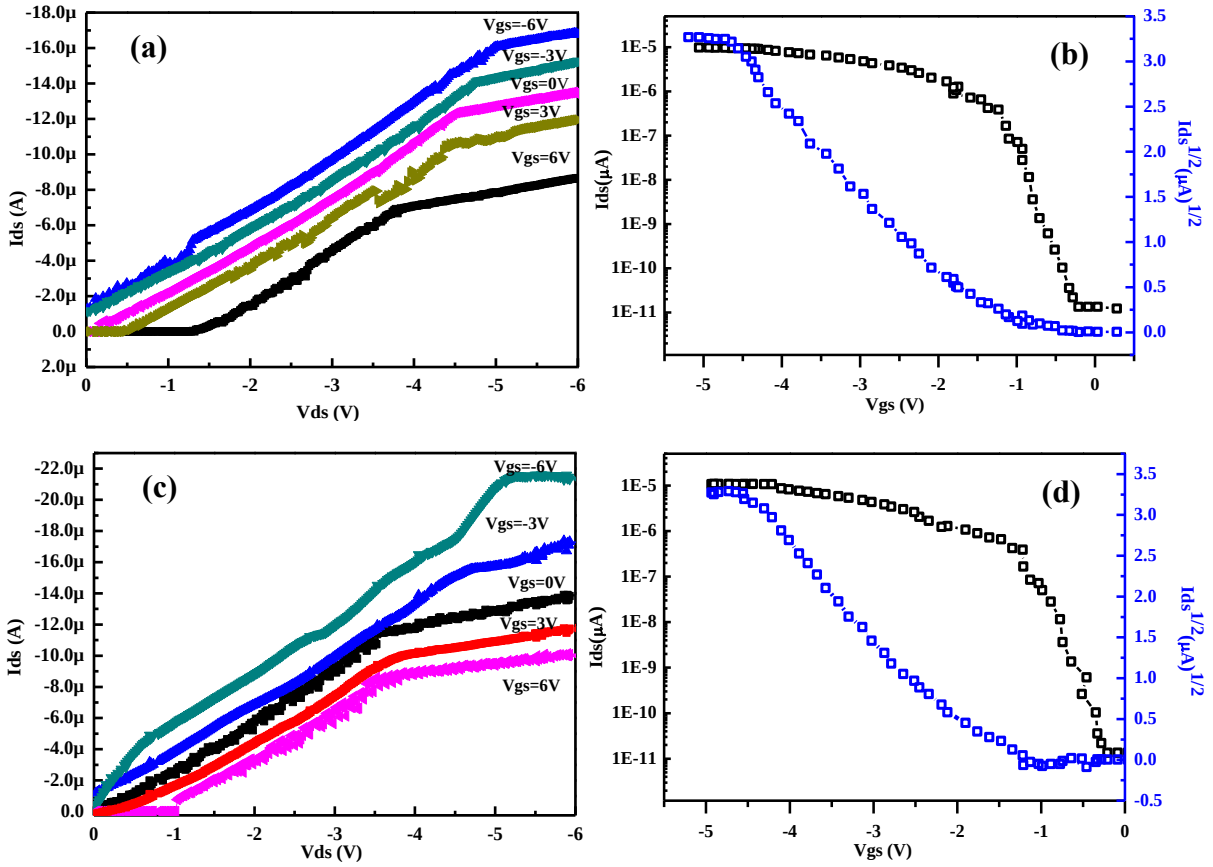


Figure S8. Electrical characteristics of the Ag/**D2**/PMMA/ITO, OFETs on glass substrate at 25°C and 50 °C; (a) output characteristics of Ag/**D2**/PMMA/ITO at 25 °C, where V_{ds} was swept from 0 to –6 V at V_{gs} varied from 6 to –6 V with the step of 3 V; (b) I_{ds} vs V_{gs} (logarithmic and linear scale) at V_{ds} = –6 V for gate voltage varying from –5 V to 0 V for Ag/**D2**/PMMA/ITO at 25 °C; (c) output characteristics of Ag/**D2**/PMMA/ITO at 50 °C, where V_{ds} was swept from 0 to –6 V at V_{gs} varied from 6 to –6 V with the step of 3 V; (d) I_{ds} vs V_{gs} (logarithmic and linear scale) at V_{ds} = –6 V for gate voltage varying from –5 V to 0 V for Ag/**D2**/PMMA/ITO at 50 °C.

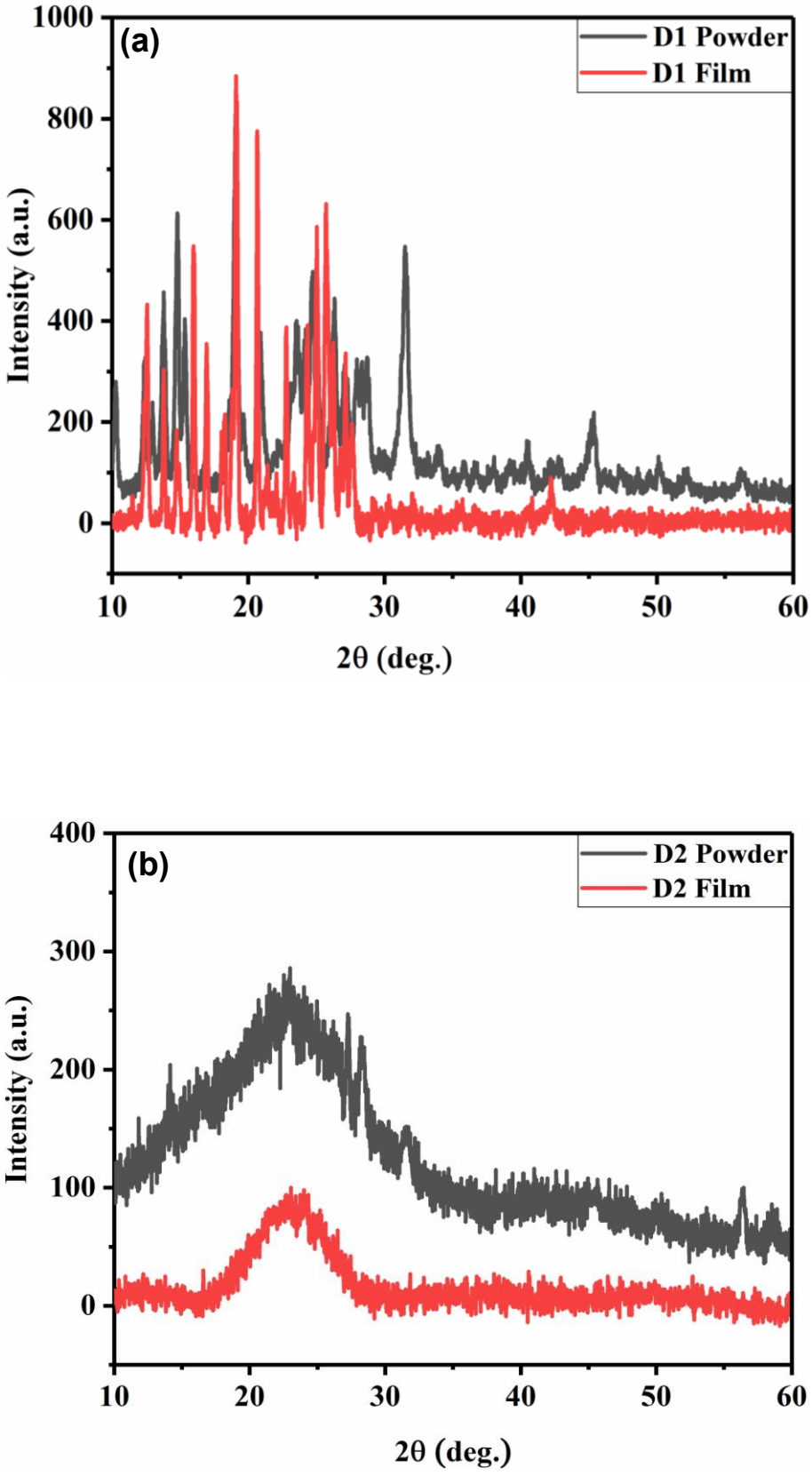


Figure S9. XRD patterns of powder and thin-films of (a) **D1** and (b) **D2**.

References

1. A. L. Spek, *Acta Crystallogr. Sect. D.* 2009, **65**, 148.
2. A. L. Spek, PLATON–A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2005
3. C. Janiak, *J. Chem. Soc. Dalton Trans.* 2000, 3885.
4. A. Tahli, Ü. Köc, R. F. M. Elshaarawy, A. C. Kautz and C. Janiak, C*rystals*. 2016, **6**, 23.
5. A. H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, ¨ O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT, 2009.