Ordered Arrays of Gold Nanoparticles Crosslinked by Dithioacetate Linkers for Molecular devices

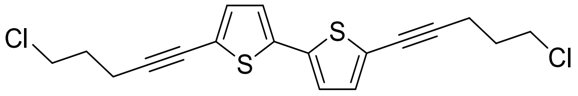
Maryana Asaad, [a*] Andrea. Vezzoli [b], Abdalghani Daaoub [c], Joanna Borowiec [d], Eugenia Pyurbeeva [a], Hatef Sadeghi [c], Sara Sangtarash [c], Simon J. Higgins [b], and Jan. A. Mol [a]

Synthesis of the di(SAc) molecules

The synthesis of 5[Ph]5 and 5[T3]5 are reported elsewhere.[1, 2] 5[T2]5 was prepared by Sonogashira cross-coupling of 5,5'-dibromo-2,2'-bithiophene and 5-chloro-1-pentyne, followed by hydrogenation and reaction with potassium thioacetate.

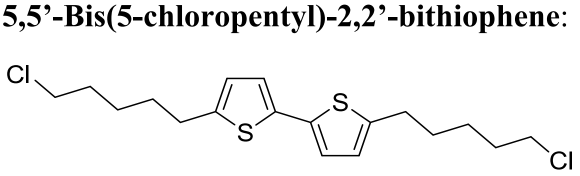
All reactions were performed under inert atmosphere, in dry solvents and in oven-dried glassware. All reagents were purchased from Sigma-Aldrich / Merck, and all solvents were purchased from ThermoFisher scientific. Chromatography was performed on Merck Silica Gel 60 F-254 plates and Sigma-Aldrich technical grade silica (230-400 mesh, pore size 60 Å). NMR spectra were recorded using a Bruker Avance 400 Ultrashield spectrometer and referenced to internal TMS; chemical shifts are reported as ppm, and coupling constants in Hz. HRMS spectra were recorded with an Agilent Q-TOF 7200 spectrometer.

5,5'-Bis(5-chloropent-1-yn-1-yl)-2,2'-bithiophene:



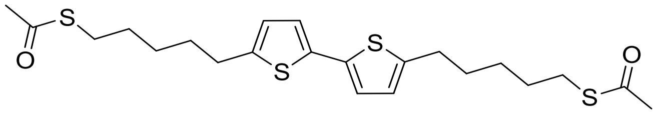
DIPA:THF (1:1, 40 mL) was degassed by bubbling Ar through for 30 minutes prior to the addition of 5,5'-dibromo-2,2'-bithiophene (2 g, 6.21 mmol), $PdCl_2(MeCN)_2$ (80 mg, 0.3 mmol), PPh_3 (242 mg, 0.6 mmol) and CuI (45 mg ,0.23 mmol). After flushing with Ar for additional 10 minutes, 5-chloro-1-pentyne (1.9 g, 18.51 mmol) was added and the reaction was heated to 65 °C under Ar and stirred for 16 hours. The resulting suspension was then allowed to cool down to room temperature and filtered. The residue was washed with 3x20mL CH_2Cl_2 and the solvent was then removed in vacuo. The crude product was purified by flash chromatography on silica (10 % CH_2Cl_2 in hexanes as eluant) to give the title compound as a pale yellow powder (1.97 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (dd, 4H, J = 11.6, 3.8, Th), 3.69, (t, 4H, J = 6.4, CH_2), 2.64 (t, 4H, J = 6.8, CH_2), 2.06 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 132.6, 123.9, 123.2, 94.1, 74.8, 44.1, 31.6, 17.6. m/z (HRMS, CI, CH_4) 367.0144 [M+H]+, $C_{18}H_{17}Cl_2S_2$ calc. 367.0149.

5,5'-Bis(5-chloropentyl)-2,2'-bithiophene:



5,5'-Bis(5-chloropent-1-yn-1-yl)-2,2'-bithiophene (1.665 g, 4.53 mmol) was subjected to catalytic hydrogenation (60 mL MeOH, 50 mg Pd/C 10%, H_2 atmosphere, 48 h, room temperature). The resulting solution was filtered through a bed of celite, and the solvent removed in vacuo to a brown oil. The crude product was purified by flash chromatography on silica (10% CH_2Cl_2 in hexanes as eluant) to obtain an impure yellow oil. The title compound was obtained in higher purity as a pale-yellow powder by recrystallisation from boiling EtOH (1.612 g, 97 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.89 (d, 2H, J = 3.5, Th), 6.65 (d, 2H, J = 3.8, Th), 3.54 (t, 4H, J = 6.7, CH_2), 2.79 (t, 4H, J = 7.5, CH_2), 1.81 (m, 4H, CH_2), 1.71 (m, 4H, CH_2), 1.52 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 135.8, 125.2, 123.1, 45.3, 32.8, 31.3, 30.4, 26.7. m/z (HRMS, CI, CH_4) 375.0754 [M+H]+, $C_{18}H_{25}Cl_2S_2$ calc. 375.0775.

S,S'-([2,2'-bithiophene]-5,5'-diylbis(pentane-5,1-diyl)) diethanethioate (5[T2]5):



A solution of 5,5'-bis(5-chloropentyl)-2,2'-bithiophene (1.5 g, 4 mmol), sodium iodide (300 mg, 2 mmol) and KSAc (1.48 g, 13 mmol) in acetone (40 mL) was refluxed under Ar atmosphere for 18 hours. The resulting orange suspension was filtered, the residue washed with cold acetone and the combined filtrates were concentrated in vacuo. The obtained crude product was purified by flash chromatography on silica (CH_2Cl_2 as eluant) and recrystallised from boiling EtOH to give the title compound as a pale yellow microcrystalline powder (1.49 g, 79 %). Found: C = 58.01, H = 6.45, S = 28.97 %. $C_{22}H_{30}O_2S_4$ requires C = 58.11, H = 6.65, S = 28.21 %. ^{1}H NMR (400 MHz, CDCl3): δ = 6.98 (d, 2H, J = 3.6, Th), 6.64 (d, 2H, J = 3.6, Th), 2.87 (t, 4H, J = 7.2, CH_2), 2.78 (t, 4H, J = 7.7, CH_2), 2.31 (s, 6H, CH_3), 1.73 – 1.56 (m, 8H, CH_2), 1.44 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1, 144.2, 132.3, 124.8, 122.7, 31.0, 30.7, 29.9, 29.3, 28.9, 28.1. m/z (HRMS, CI, CH_4) 455.1204 [M+H]+, $C_{22}H_{31}O_2S_4$ calc. 455.1207.

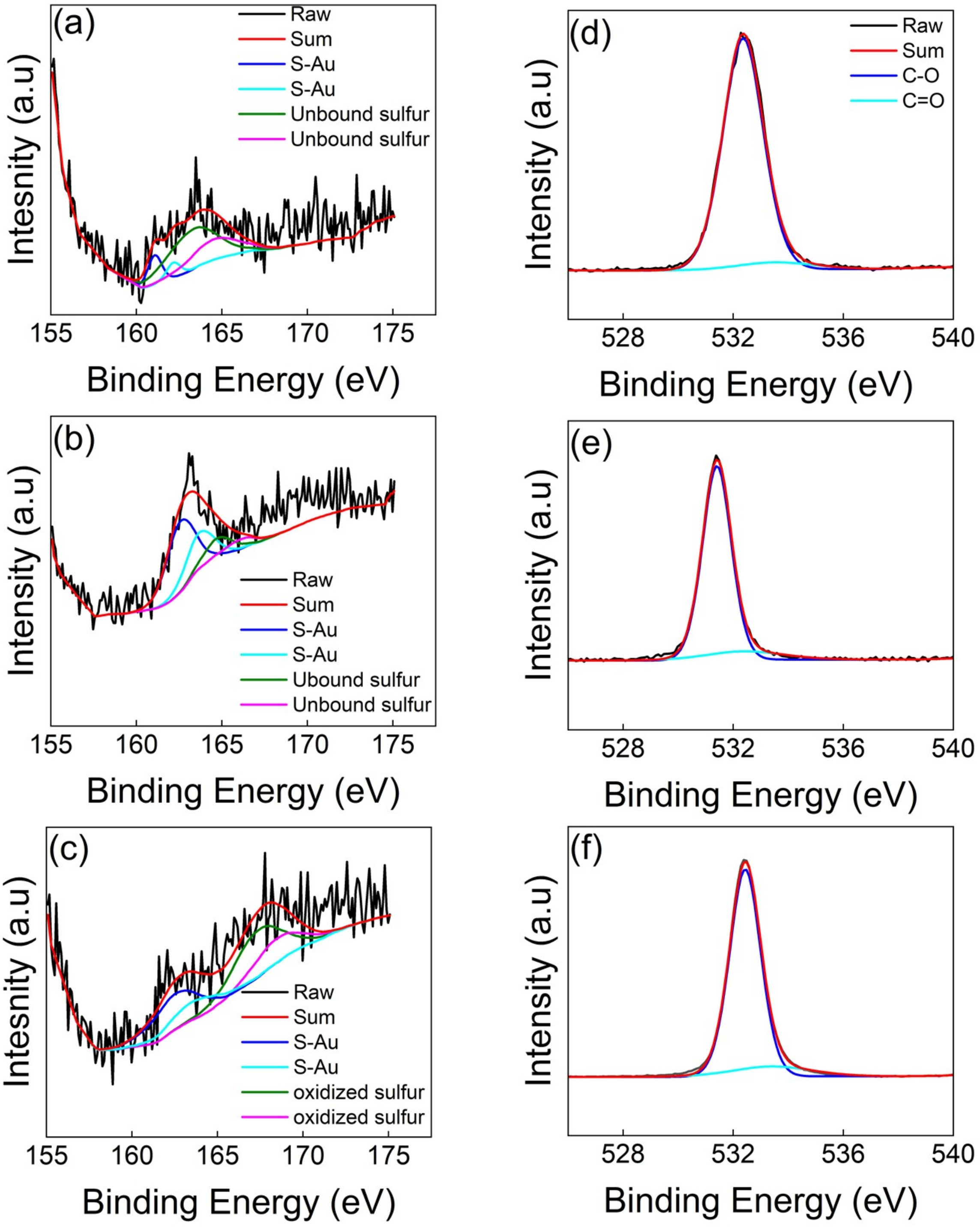


Figure S1. S 2sp3 (**a**, **b**, **c**) and O 1S (**e**, **f**, **d**) XPS signals for SAMs from AuNPs functionlised with 5[T3]5 (**a**, **d**), 5[T2]5 (**b**, **e**), and 5[Ph]5 (**c**, **f**).

Table S1. Summary of the observed binding energy positions for the C 1s and Au 4f core levels for the SAMs prepared using 5[T3]5, 5[T2]5, and [5[Ph]5.

Sample	Au 4f$_{7/2}$	Au 4f$_{5/2}$		C 1s	
	B.E. (eV)	B.E. (eV)	Assignation	B.E. (eV)	Assignation
AuNPs/5T35	83.67	87.35	Au^0	284.5	C-C/C-H
	84.68	88.26	Au-S	283.54	C=C
				285.92	C-O/C-S
AuNPs/5T25	82.79	86.50	Au^0	283.88	C-C/C-H
	83.55	87.25	Au-S	283.1	C=C
				285.37	C-O/C-S
AuNPs/5[ph]5	83.11	86.78	Au^0	285.67	C-C/C-H
	83.24	86.82	Au-S	284.07	C=C
				287.19	C-O/C-S

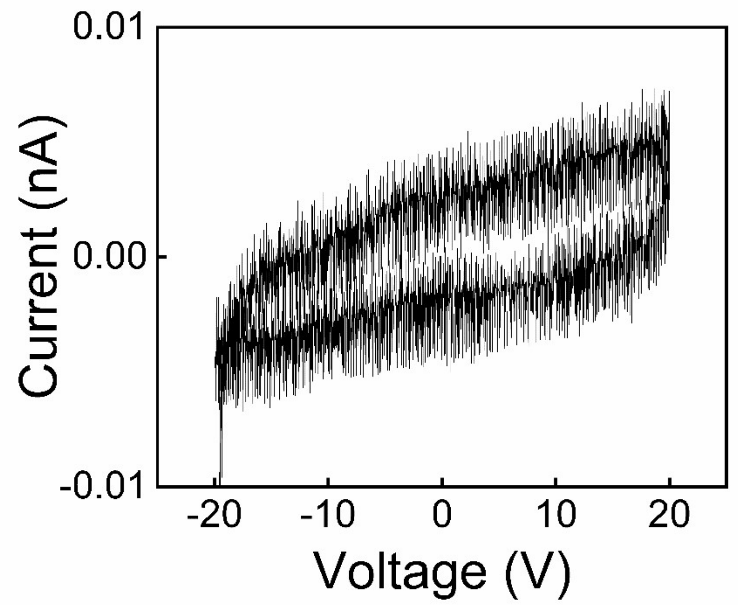


Figure S2. *IV* sweep of a bare device.

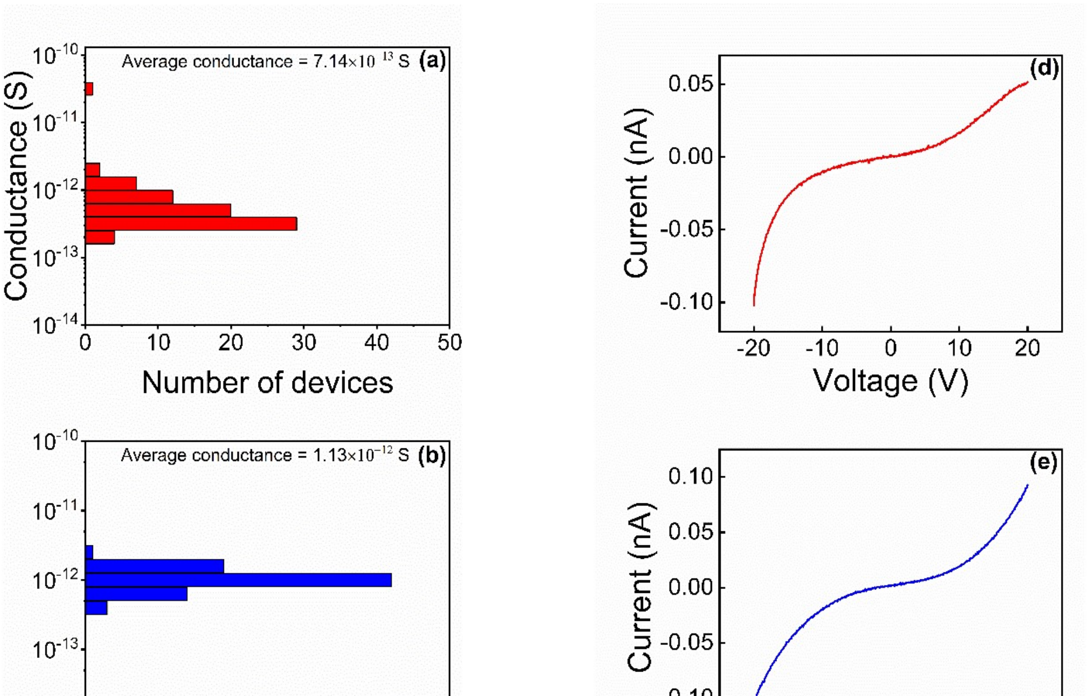


Figure S3. Conductance of the di(SAc) molecules without AuNPs versus occurrence in a log-normal histogram for 5[ph]5 (76 devices) **(a)**, 5[T2]5 (79 devices) **(b)**, 5[T3]5 (80 devices) **(c)**. The average conductance values were obtained from fitting the histograms to Gaussian functions. *IV* relation of a representative device for 5[Ph]5 **(d)**, 5[T2]5 **(e)** and 5[T3]5 **(f)**. Devices were prepared by drop casting 5µL of a solution of the desired molecules (2 µmol of the desired surfactant in10 mL hexane) on a substrate.

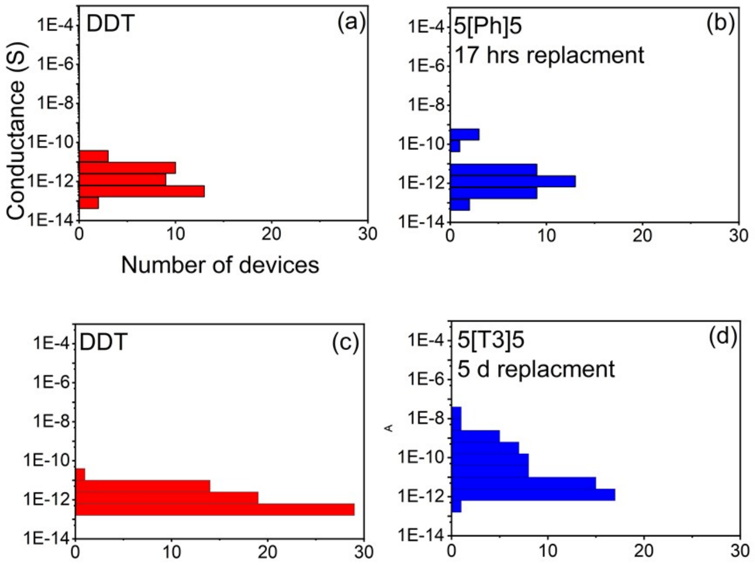


Figure S4. Conductance of SAM AuNPs versus occurrence in a log-normal histogram pre-exchange (a, c) and post-exchange for 5[Ph]5 (b,), 5[T3]5.

Theoretical methods

The optimised geometry, ground state Hamiltonian and overlap matrix element of each structure was self-consistently obtained using the SIESTA implementation of density functional theory (DFT).[3] SIESTA employs norm-conserving pseudopotentials to account for the core electrons, and linear combinations of atomic orbitals to construct the valence states. The generalised gradient approximation (GGA) of the exchange and correlation functional is used with the Perdew-Burke-Ernzerhof parameterisation (PBE) a double-ζ polarised (DZP) basis set, a real-space grid defined with an equivalent energy cut-off of 250 Ry. The geometry optimisation for each structure is performed to achieve forces smaller than 10 meV / Å.

The mean-field Hamiltonian obtained from the converged DFT calculation was combined with Gollum implementation[4] of the non-equilibrium Green's function method [5] to calculate the phase-coherent, elastic scattering properties of each system consisting of left gold (source) and right gold (drain) leads and the scattering region. The transmission coefficient $T(E)$ for electrons of energy E (passing from the source to the drain) is calculated via the relation: $T(E) = Trace\left(\Gamma_R(E)G^R(E)\Gamma_L(E)G^{R\dagger}(E)\right)$. In this expression, $\Gamma_{L,R}(E) = i\left(\Sigma_{L,R}(E) - \Sigma_{L,R}{}^{\dagger}(E)\right)$ describe the level broadening due to the coupling between left (L) and right (R) electrodes and the central scattering region, $\Sigma_{L,R}(E)$ are the retarded self-energies associated with this coupling and $G^R = (ES - H - \Sigma_L - \Sigma_R)^{-1}$ is the retarded Green's function, where H is the Hamiltonian and S is overlap matrix. Using obtained transmission coefficient $T(E)$, the conductance could be calculated by Landauer formula ($G = G_0 \int dE\,T(E)(-\partial f/\partial E)$) where $G_0 = 2e^2/h$ is conductance quantum.

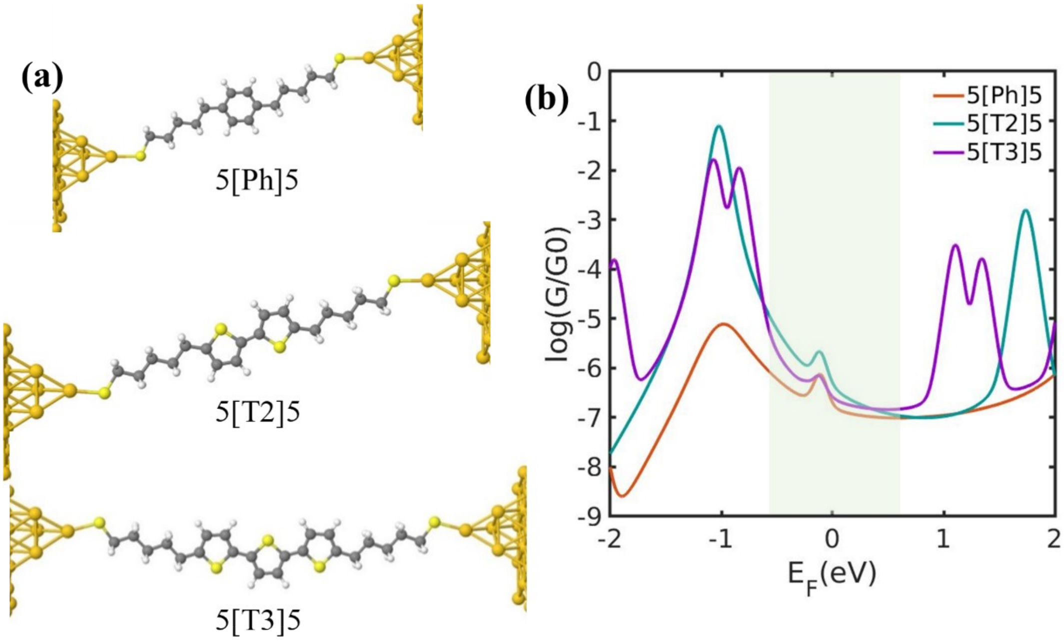
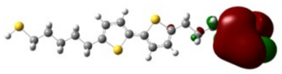
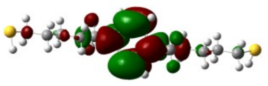
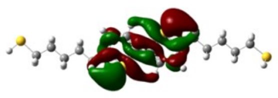
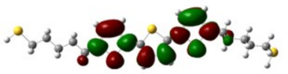
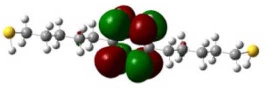
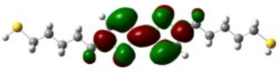
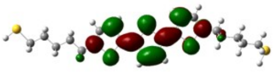
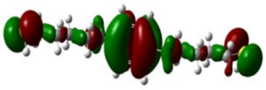
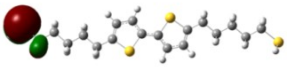
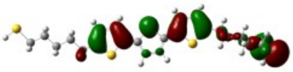
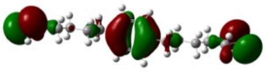
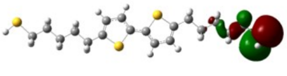
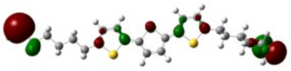


Figure S5. **(a)** Relaxed structure of molecular junctions, **(b)** Average of calculated electrical conductance (for 5 different binding configurations) versus electrode energy for 5[Ph]5, 5[T2]5 and 5[T3]5

Table S2. Frontier molecular orbitals and energies of the 5[Ph]5, 5[T2]5 and 5[T3]5 molecules, respectively. Units are eV.

Structure/Orbital	**5[Ph]5**	**5[T2]5**	**5[T3]5**
LUMO+2	0.17 	0.10 	-0.06 
LUMO+1	-0.24 	0.01 	-0.80 

LUMO	**-0.29** 	**−1.58** 	**-2.08** 
HOMO	**-6.53** 	**−5.61** 	**-5.36** 
HOMO-1	-6.64 	−6.68 	-6.63 
HOMO-2	-6.69 	−6.67 	−6.67 

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