Photo-modulable Molecular Transport Junctions based on Organometallic Molecular Wire

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Supplementary Information

Processes of *1o* synthesis:

The reactions were achieved under an inert atmosphere, using Schlenk techniques. Solvents were freshly distilled under argon using standard procedures. The diethynyl-substituted dithienylethene,[S1] AcS-*p*-C_6H_4–C≡CH,[S2] and the ruthenium precursor, [(dppe)$_2$RuCl](OTf),[S3] were prepared as previously reported. All the reactions and handling of the compound were carried out in the dark. High resolution mass spectra (HRMS) were recorded in Rennes at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest) on a ZabSpecTOF (LSIMS at 4 kV) spectrometer.

***trans*-[(dppe)$_2$(Cl)Ru=C=CH-*p*-C_6H_4-SAc)](OTf)**. In a Schlenk tube, [(dppe)$_2$RuCl][OTf] (1.863 g, 1.75 mmol) and AcS-*p*-C_6H_4-C≡CH (363 mg, 2.06 mmol) were pumped for 30 minutes. Then, well degassed dichloromethane (100 mL) was transferred onto the solids. The solution was stirred for 24 hours at room temperature and then evaporated. The residue was dissolved in dichloromethane (30 mL) and further slow addition of pentane (70 mL) led to a light green precipitate. After filtration, the residue was washed with ether (2 × 50 mL) to yield to 2.05 g of a light green solid (95% yield). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 297 K): δ = 36.1 (s, PPh_2). ^1H NMR (300 MHz, $CDCl_3$, 297 K): δ = 7.37-7.08 (m, 40H, H_{Ar}), 6.57 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2H, -C_6H_4-S), 5.67 (d, 2H, $^3J_{H\text{-}H}$ = 9.0 Hz, -C_6H_4-S), 4.49 (br., 1H, Ru=C=CH), 2.94 (m, 8H, P-CH_2), 2.36 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 297 K, δ (ppm)): 353.01 (quint., Ru=C, $^2J_{(P,C)}$ = 13 Hz), 193.88 (C=O), 134.30 (*m*-C_6H_4-$SCOCH_3$), 134.09 and 133.31 (*o*-C_6H_5), 131.52 and 130.93 (*p*-C_6H_5), 131.28 (m, *ipso*-C_6H_5), 128.85 and 128.11 (*m*-C_6H_5), 127.87 (*p*-C_6H_4-$SCOCH_3$), 127.62 (*o*-C_6H_4-$SCOCH_3$), 125.33 (*ipso*-C_6H_4-$SCOCH_3$), 108.81 (Ru=C=$\underline{C}$H), 29.99 (s, CO$\underline{C}$H3), 28.60 (m., CH_2 (dppe), $|^1J_{(P,C)} + {}^3J_{(P,C)}|$ = 22 Hz). IR (KBr): ν = 1705 cm^{-1} (C=O), 1633 cm^{-1} (C=C). HR-MS FAB+ (m/z): 1109.1768 ([M+] calcd: 1109.1734). Elemental analysis (%) for $C_{63}H_{56}ClF_3O_4P_4RuS_2$, 0.33 CH_2Cl_2: C 58.79, H 4.58, S 4.74 (calcd: C 58.59, H 4.62, S 4.79).

***trans*-[AcS-*p*-C_6H_4-C≡C-(dppe)$_2$Ru-C≡C-(DTE)-C≡C-Ru(dppe)$_2$-C≡C-*p*-C_6H_4-SAc] (*1o*).** In a Schlenk tube, complex **1** (368 mg, 0.29 mmol) , $NaPF_6$ (98 mg, 0.58 mmol), and the diethynyl-substituted dithienylethene compound HC≡C-(DTE)-C≡CH (60 mg, 0.15 mmol) were pumped for 30 min. Then, dichloromethane (20 mL) mixed together with triethylamine (0.39 mL, 2.92 mmol) was saturated with argon and transferred into the Schlenk tube. More triethylamine (0.39 mL, 2.92 mmol) was further added. The mixture was stirred for five days in the dark, and then the solvent was evaporated. The residue was solved in dichloromethane (15 mL), washed with degassed water (3 × 15 mL), and the solvent was evaporated. The residue was dissolved in dichloromethane (15 mL) and further slow addition of pentane (60 mL) led to a light green precipitate. The product was further purified via filtration on small alumina plugs (elution with dichloromethane) to obtain 220 mg of compound as a greyish solid (59% yield). ^{31}P NMR (81 MHz, CD_2Cl_2, 297 K): δ = 53.6 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$, 297 K): δ = 7.69-6.83 (m, 88 H, Ph), 6.27 (s, 2 H, H_{DTE}), 2.62 (m, 16 H, PCH_2CH_2P), 2.44 (s, 6H, $COCH_3$), 1.82 (s, 6 H, $CH_{3\ DTE}$). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 297 K, δ (ppm)): 194.95 (C=O), 140.65 (quint., Ru-C, $^2J_{(P,C)}$ = 15 Hz), 136.93 and 136.61 (m, *ipso*-C_6H_5), 135.86 (DTE), 134.34 and 133.83 (m, *o*-C_6H_5), 133.90 (*m*-C_6H_4-*p*-$SCOCH_3$), 131.58 (DTE), 130.40 (*o*-C_6H_4-$SCOCH_3$), 129.62 (*p*- C_6H_4-*p*-$SCOCH_3$), 128.94 and 128.64 (*p*-C_6H_5), 127.12 (*m*-C_6H_5), 124.14 (DTE), 124.03 (DTE), 121.44 (*ipso*-C_6H_4-$SCOCH_3$), 117.23 (Ru-C≡$\underline{C}$-Ph), 107.26 (Ru-C≡$\underline{C}$-DTE), 31.39 (m, $|^1J_{PC} + {}^3J_{PC}|$ = 23 Hz, CH_2), 29.83 (CO$\underline{C}$H3), 14.38 (CH_3 DTE). IR (KBr): ν = 1704 cm^{-1} (C=O), 2050 cm^{-1} (C≡C). HR-MS FAB$^+$ (m/z): 2560.3948 ([M^+], calcd: 2560.3901). Elemental analysis (%) for $C_{143}H_{118}F_6O_2P_8Ru_2S_4.2CH_2Cl_2$: C 63.78, H 4.50, S 4.70 (calcd: C 63.73, H 4.43, S 4.59).

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Data for *1c*: ^{31}P NMR (121 MHz, C_6D_6, 297 K): δ 52.8 (s, PPh_2). ^{1}H NMR (300 MHz, C_6D_6, 297 K): δ 7.78-6.88 (m, 88 H, Ph), 5.71 (s, 2 H, ArH), 2.63 (s, 6 H, $ArCH_3$), 2.43 (m, 16 H, PCH_2CH_2P) 1.89 (s, 6 H, $COCH_3$). IR (KBr): ν = 2016 cm^{-1} (C≡C).

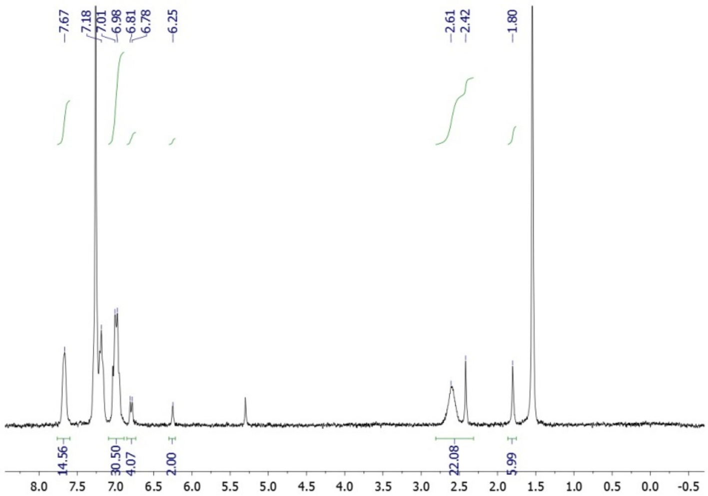

Fig. S1. ^{1}H NMR spectrum of ***1*** in $CDCl_3$.

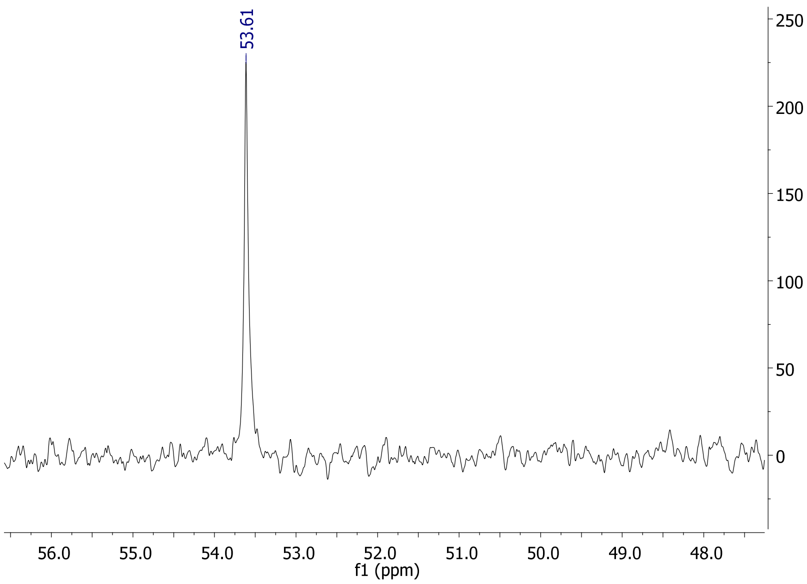

Fig. S2. ^{31}P NMR spectrum of ***1*** in $CDCl_3$.

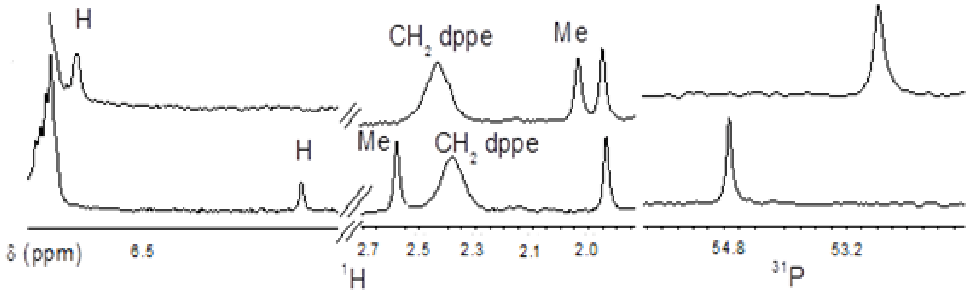

Fig. S3. Selected ^{31}P and ^{1}H NMR signals in C_6D_6 of ***1o*** (up) and of ***1c*** (bottom) after excitation at λ= 350 nm in the NMR tube. The initial spectra were recovered after bleaching at λ= 750 nm**.**

Experimental Section

OWL-generated nanogap preparation: OWL-generated nanogaps were prepared by electrochemically deposition using an anodic aluminum oxide (AAO) porous membrane (Whatman, Anodisc 0.02 µm pores, 47 mm outer diameter) as a template. AAO membranes were evaporated with 200 nm of Ag metal on the reverse, and then placed in an electrochemical cell, which contained a Pt counter electrode and an Ag/AgCl reference electrode. In all experiments, commercially available 1025 Silver (Ag) and Nickel Sulfamate RTU (Ni) and Orotemp 24RTU (Au) electroplating solutions (Technic Inc.) were used for electrochemical deposition (EC epsilon, BASi, West Lafayette, IN, USA). Ag was deposited as an initial electrical contact layer under DC current at -800 mV (*vs*. Ag/AgCl), nickel was plated at -850 mV, while gold was plated at -950 mV. We obtained ~3 nm thick nickel layer by controlling the charge (30 mC) during the electrochemical deposition of nickel. Plasma enhanced chemical vapor deposition (PECVD) was used to deposit ~50 nm silica on the wire surface. After etching the sacrificial layer of Ni by 1 M HCl for 3 hours, a ~3 nm nanogap was generated for the assembly of ***1*** molecules within.

Device fabrication: First, microelectrodes were formed via photolithography by three steps. 1) Si wafers with 600 nm SiO_2 layer were cleaned via sonication in acetone and ethanol for 30 min, rinsed with ethanol and dried with N_2, and then placed in an oven (95 °C) for 5 min after spin coating with a photoresist (AZ 1518 Photoresist, Shipley, USA) at 500 rpm for 5s and 4500 rpm for 45 s. 2) The resist was subsequently patterned using a mask aligner (SUSS MJB4 Mask Aligner, Garching, Germany) and developed with AZ 300 MIF. 3) Cr (8 nm) and Au (50 nm) were thermally evaporated onto the patterned wafer and the wafer was immersed in acetone for liftoff. Subsequently, a suspension of gold nanorods with OWL-fabricated nanogaps was deposited on a chip containing prefabricated Au microelectrodes. Electron beam lithography (EBL) was employed to define an inner electrode pattern that connects the nanorods with the microelectrodes. A resist layer of PMMA was prepared by the following procedure: 950 PMMA C7 was spin-coated at 500 rpm (10 second) and 3000 rpm (45 second) followed by baking at 180 °C for 4 min. EBL was carried out using a SEM (JEOL JSM-6360 SEM, Tokyo, Japan), equipped with the Raith SEM lithography kits (Raith ELPHY Quantum, Dortmund, Germany) at 30 kV acceleration voltage and 40 pA beam current. Cr (10nm) and Au (400 nm) were then thermally evaporated onto the e-beam resist-coated substrate after it had been developed with 1:3 (v/v) MIBK/IPA solution for 30 s, and then rinsed with IPA. Finally, the two ends of the nanorod were connected with the microelectrodes. These nanogap devices were ready for assembly of functional molecules, and electrical measurement. SEM (JEOL JSM-7600F SEM, Tokyo, Japan) was employed to observe the morphology of the nanodevices and measure the size of the nanogap.

1c assembly into the nanogap: The fabricated nanogap devices were cleaned by oxygen plasma for 1 min to remove organic contamination on the wafer surface, followed by cleaning in ethanol and drying with N_2. The wafer was then immersed in the degassed THF solution (5ml) of ***1c*** (1mg) in the dark for 24 hours under N_2 atmosphere. This ***1c***/THF solution was obtained by the following method: 1) The THF solution of precursor ***1o*** was irradiated with 365 nm UV light for 30min to ensure that all the precursor ***1o*** switched to precursor ***1c;*** 2) to the degassed solution of precursor ***1c*** NH_4OH (28% of NH_3, 5 μL) was added dropwise for deprotection of the thiol; 3) the solution was stirred for 10 min at room temperature under N_2. Finally, the wafer with nanogap devices was removed from the solution and rinsed with THF and ethanol, and then blown dry with N_2.

Electrical Measurements: The photo-controllable current-voltage characteristics and current- time curves of the devices were obtained using a semiconductor parameter analyzer (Keithley 4200-SCS, Cleveland, OH, USA) for application of potentials and measurement of currents, combined with a closed cycle cryogenic wafer probe station (Lakeshore CRX-4K, Westerville, OH, USA) for connecting the microelectrodes. In typical experiments, the measurements were conducted under vacuum (5×10^{-5} torr) and UV-vis irradiation were performed with 150 W xenon lamp with single wavelength light filters at 365 nm and 700nm.

Computational Details

Density functional theory (DFT) calculations were performed with the Amsterdam Density Functional package (ADF 2010.02)[S4] on slightly simplified models of ***1o*** and ***1c*** (i.e., phenyl groups replaced by hydrogen atoms). The geometries were fully optimized without constraints (C_1 symmetry). The bonding energies and Cartesian coordinates of each structure are given in Table S1. Due to the size of the molecules and resulting computational limits, frequency analyses were not performed but the convergence criteria were nonetheless stricter than usual (energy 0.0005 ua, displacement 0.005 Å). Geometry optimizations were performed on ***1c*** by imposing the S-S distance to be that of the relaxed ***1o***, and on ***1o*** by imposing the S-S distance to be that of the relaxed ***1c*** (see Table S1).

Electron correlation was treated using the local density approximation (LDA) with the Vosko-Wilk-Nusair parametrization.[S5] The non-local corrections (GGA) of Becke and Perdew were added to the exchange and correlation energies, respectively.[S6] The analytical gradient method implemented by Verluis and Ziegler was additionally used.[S7] The standard ADF TZP basis was set, i.e., triple-ξ STO basis set for the valence core augmented with a 3d polarisation function for C, P was used. Orbitals up to 1s, 2p, and 4p were kept frozen for C, P, and Ru, respectively. In order to evaluate the steric hindrance due to phenyl groups of the dppe ligands, non-optimized structures were built on the basis of the optimized simplified structures (see Figure 4 and Figure S8). Bi-coordination of ***1o*** on the same gold surface is unambiguously impossible due to the phenyl groups.

We used the ATK2008.10 package[S8] to compute the Non-Equilibrium Green function of the device with DFT Hamiltonian at the GGA.revPBE level.[S9] We used the SIESTA[S10] scheme with SZP numerical orbital basis set for valence electrons of gold atoms and DZP for valence electrons of molecular atoms, a (9,9,100) Monkhosrt-Pack k-sampling, and a 300Ry mesh cut-off. Five layers of gold were included on each side of the molecule in the scattering region to soften the transition of the electrostatic potential from the bulk to the (111) chemisorbed gold surface. The

Au-S bond distance between the molecule and gold is about 2.42 Å in the chosen on-top configuration. The MPSH states are projected on the molecular part connected to the two gold layers.

Table S1. Optimized Cartesian coordinates of ***1o*** and ***1c*** fully relaxed or constrained (see text)

1o				***1o* S-S distance constrained at 34.2 Å**			
E = -645.871 eV				E = -645.844 eV			
C	-2.224198	1.932926	-1.463540	C	7.742629	-7.695870	-10.853500
C	-1.483219	0.785218	-1.896879	C	7.111619	-6.493821	-11.250583
C	-2.121912	0.077690	-2.916185	C	7.199254	-6.143724	-12.618848
S	-3.620155	0.848600	-3.336964	C	7.873901	-6.945270	-13.534805
C	-3.409016	2.143890	-2.142164	C	8.489279	-8.137075	-13.119103
C	-0.236770	0.363833	-1.258018	C	8.415670	-8.503418	-11.766564
C	-0.105609	0.477316	0.241826	C	6.414684	-5.672708	-10.317030
C	1.071942	-0.471211	0.609757	C	5.799136	-4.959413	-9.515456
C	1.880648	-0.567390	-0.718728	Ru	4.746309	-3.733843	-8.167671
C	0.917475	-0.144167	-1.802966	P	6.248151	-1.983460	-8.632102
F	0.219553	1.775010	0.632764	C	7.836900	-2.236250	-7.666399
F	-1.239332	0.147842	0.935494	C	7.514895	-2.821753	-6.283512
F	0.572697	-1.702068	0.940560	P	6.288823	-4.230458	-6.462170
F	1.816328	-0.026027	1.658331	S	9.323286	-9.123083	-14.356459
F	2.380531	-1.845817	-0.879912	C	3.704224	-2.510740	-6.823840
F	2.983031	0.261678	-0.654142	C	3.113350	-1.782491	-6.014474
C	1.344302	-0.196779	-3.205929	C	2.463065	-0.946840	-5.092599
C	2.005265	-1.324635	-3.792399	C	2.008866	-1.219758	-3.816037
C	2.389504	-1.148398	-5.108667	C	1.380508	-0.115480	-3.155770
S	1.932121	0.485171	-5.623710	C	1.366073	1.043896	-3.932951
C	1.231472	0.882345	-4.084476	S	2.117995	0.750029	-5.472392
C	3.050842	-2.018798	-5.990486	C	0.886597	-0.175781	-1.775680
C	3.655429	-2.735299	-6.800698	C	-0.270335	0.331264	-1.235515
Ru	4.722410	-3.914209	-8.166876	C	-0.209878	0.284250	0.273127
C	5.806874	-5.075664	-9.548880	C	0.904099	-0.753215	0.593908
C	0.679480	2.255792	-3.852393	C	1.775081	-0.750483	-0.697260
C	-1.728878	-1.203351	-3.585468	C	-1.464999	0.877703	-1.877329
C	-4.375538	3.154612	-2.014921	C	-2.191491	1.983273	-1.326851
C	-5.285053	3.994342	-1.958080	C	-3.342809	2.317152	-2.013041
Ru	-6.823579	5.417262	-1.978640	S	-3.535191	1.202735	-3.380202
C	-8.378762	6.831569	-2.104461	C	-2.079684	0.332218	-3.006210
P	3.304644	-5.753696	-7.806850	C	-1.699738	-0.864384	-3.822775
C	2.094443	-5.903780	-9.232566	C	-4.299368	3.312935	-1.760353
C	1.659301	-4.504128	-9.691717	C	-5.198328	4.140326	-1.555284
P	3.162396	-3.389607	-9.845369	Ru	-6.782441	5.462720	-1.195996
P	6.278945	-4.428281	-6.478909	P	-6.979114	5.973042	-3.482417
C	7.489498	-3.009137	-6.274925	C	-6.213838	7.651491	-3.818771
C	7.792789	-2.384496	-7.644862	C	-4.944930	7.818667	-2.969547
P	6.193153	-2.126925	-8.590518	P	-5.286638	7.278358	-1.204177
P	-6.336442	6.049890	0.232422	F	0.151697	1.517308	0.812710
C	-7.146570	4.856411	1.434620	F	-1.390177	-0.059432	0.877283
C	-8.503438	4.399489	0.878313	F	0.335081	-1.986021	0.768367
P	-8.321372	3.938490	-0.931111	F	1.610951	-0.456110	1.718247
P	-5.346394	6.915681	-3.030471	F	2.231937	-2.027132	-0.964978
C	-5.222634	6.504764	-4.856831	F	2.905047	0.017690	-0.495541
C	-6.594827	6.054536	-5.380169	C	0.870438	2.417231	-3.597374
P	-7.347584	4.814627	-4.191111	P	3.297941	-5.541570	-7.766423
H	2.186208	-2.256183	-3.264477	C	2.101773	-5.715745	-9.200580
H	0.877329	2.582532	-2.821869	C	1.685347	-4.323816	-9.698964
H	-0.412368	2.285368	-3.997731	P	3.200454	-3.226812	-9.864414
H	1.134557	2.985427	-4.534644	C	-8.382042	6.791235	-0.873195
H	1.233979	-6.523742	-8.945380	C	-9.321897	7.580333	-0.718170
H	3.783055	-7.094904	-7.724549	C	-10.403699	8.491674	-0.542944
H	2.429951	-5.789765	-6.678169	C	-11.574234	8.405949	-1.333020
H	2.642541	-6.422673	-10.034159	C	-12.630835	9.296824	-1.170474
H	1.011484	-4.031177	-8.937262	C	-12.559107	10.317148	-0.208562
H	1.108398	-4.540546	-10.641597	C	-11.408571	10.418912	0.588190
H	2.531868	-2.114659	-9.958722	C	-10.355778	9.522394	0.424162
H	3.511328	-3.559676	-11.219077	S	-13.947081	11.436325	-0.071041
H	5.839985	-0.797177	-8.209175	P	-6.628105	4.981722	1.101239
H	6.698850	-1.832568	-9.891242	C	-7.476793	3.348607	1.466611

H	8.339285	-1.436337	-7.547443	C	-8.725498	3.204531	0.583732
H	8.396420	-3.069417	-8.260295	P	-8.307807	3.673322	-1.184618
H	8.404350	-3.352876	-5.772922	H	2.114987	-2.204677	-3.371503
H	6.989331	-2.281431	-5.617184	H	1.027873	2.634570	-2.531705
H	7.158469	-5.541840	-6.635637	H	-0.209275	2.518819	-3.792975
H	5.909967	-4.657699	-5.120250	H	1.396332	3.182317	-4.182937
H	-2.606280	-1.724445	-3.989740	H	1.232127	-6.320030	-8.907615
H	-1.231184	-1.874486	-2.871218	H	3.758026	-6.885474	-7.640425
H	-1.021322	-1.030064	-4.412004	H	2.410990	-5.532860	-6.646738
H	-1.885325	2.603841	-0.678013	H	2.654050	-6.259702	-9.982405
H	-6.790376	7.309704	0.727666	H	1.033583	-3.826542	-8.963769
H	-5.012738	6.100460	0.763533	H	1.144118	-4.378828	-10.653478
H	-7.248520	5.319146	2.425907	H	2.582807	-1.948655	-10.008801
H	-6.455931	4.003464	1.524087	H	3.556600	-3.428252	-11.231970
H	-9.232346	5.224290	0.904353	H	5.912466	-0.637990	-8.292434
H	-8.914981	3.557312	1.451503	H	6.768303	-1.734211	-9.936572
H	-9.690105	3.823331	-1.315939	H	8.394234	-1.292628	-7.588777
H	-8.022174	2.544822	-0.847480	H	8.437490	-2.943765	-8.258847
H	-3.965914	7.021985	-2.687470	H	8.421240	-3.163381	-5.764865
H	-5.649042	8.310409	-3.068420	H	7.017550	-2.071862	-5.648987
H	-4.834492	7.364601	-5.420076	H	7.156047	-5.357651	-6.589194
H	-7.296896	6.902146	-5.411831	H	5.909491	-4.425305	-5.101085
H	-6.524709	5.626555	-6.389677	H	-2.572735	-1.284973	-4.338274
H	-4.490153	5.685745	-4.929715	H	-1.269656	-1.647567	-3.182693
H	-8.686234	4.753324	-4.678027	H	-0.940111	-0.615520	-4.580959
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S	9.516443	-8.940923	-14.503956	H	7.924991	-6.642960	-14.581836
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H	-13.046327	12.796270	-2.808702	H	-13.473012	12.127264	0.995353
H	9.763186	-10.038929	-13.746992	H	9.797510	-10.062443	-13.500652

1c				**_1c_ S-S distance constrained at 33.1 Å**			
E = -645.612 eV				E = -645.613 eV			
C	0.298920	10.894949	-0.142950	C	4.490444	20.668842	2.312094
C	-0.101781	9.578127	-0.435202	C	4.708931	19.554107	3.155382
C	0.971881	8.529634	-0.087639	C	5.404184	19.788090	4.364474
S	2.114956	9.423338	1.107237	C	5.858914	21.057543	4.710797
C	1.440961	11.014195	0.636786	C	5.634047	22.149266	3.858271
C	-1.261469	9.113630	-1.024814	C	4.941910	21.940152	2.654026
C	-1.540566	7.704106	-1.138724	C	4.252356	18.250967	2.800929
C	-0.761022	6.754568	-0.508578	C	3.858084	17.122790	2.482940
C	0.284432	7.271471	0.498189	Ru	3.188154	15.201418	1.939938
S	1.432903	5.805773	0.759531	P	1.957351	15.179366	3.949690
C	0.249319	4.682866	0.022852	C	0.416251	16.228743	3.751205
C	-0.801601	5.350270	-0.590705	C	-0.165202	16.034243	2.342879
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C	-3.467354	8.871987	-1.979982	S	6.193830	23.806753	4.227053
C	-2.727912	7.490521	-2.007053	C	2.527564	13.304532	1.403770
C	0.427414	3.299909	0.072034	C	2.120122	12.177238	1.075946

C	0.474016	2.057628	0.073707	C	1.644422	10.917851	0.714346
Ru	0.381555	-0.021841	0.032671	C	0.508770	10.630167	-0.029594
P	1.048845	-0.036685	-2.230719	C	0.252502	9.261254	-0.237426
C	-0.427433	0.313804	-3.335441	C	1.440657	8.359829	0.146059
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F	-2.399873	7.192111	-3.332248	C	-0.856165	8.632196	-0.770207
F	-3.574125	6.474231	-1.609041	C	-2.146723	6.796089	-1.615970
F	-4.145214	9.142820	-3.129090	C	-3.036862	8.085347	-1.655305
F	-4.373675	8.870143	-0.951607	C	-2.024344	9.264321	-1.440468
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Ru	3.186056	15.190904	1.950235	C	0.184299	7.358030	2.168795
C	3.872836	17.107367	2.497374	C	1.514563	3.140198	0.691382
P	-0.304670	-0.018370	2.285472	C	1.804582	1.938689	0.820149
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C	2.378915	-0.613894	2.804645	C	2.674270	-2.130688	1.270020
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C	6.569634	14.535071	1.577894	C	2.508408	-7.002522	2.089439
C	6.037085	14.359986	0.147767	C	3.823894	-7.472919	1.943200
P	4.426705	15.301623	-0.048826	C	4.838031	-6.561507	1.610805
P	1.213441	16.148947	1.089951	C	4.542390	-5.212819	1.432082
C	-0.155372	16.061987	2.370892	F	-1.712815	9.819862	-2.679730
C	0.435434	16.247375	3.776530	F	-2.621263	10.293986	-0.730591
P	1.964822	15.179438	3.966299	F	-3.761860	8.204849	-2.801297
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H	5.794259	13.304604	-0.051481	H	-0.150003	11.421726	-0.379990
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H	7.400538	13.847915	1.788739	H	3.152158	7.481555	-0.902115
H	6.923907	15.565368	1.736944	H	1.644500	7.508271	-1.856936

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C	-1.429170	-5.338952	0.017947	H	1.179228	17.517942	0.716851
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C	0.758707	-7.024858	-0.359977	H	2.480165	15.694111	5.171722
C	0.940226	-5.644769	-0.318365	H	5.290860	12.916665	3.080713
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S	-0.838199	-9.339122	-0.249671	H	-0.602528	15.029213	2.237178
H	1.622607	-7.674909	-0.507805	H	-0.318400	15.985347	4.531035
H	1.941996	-5.230181	-0.435170	H	0.744528	17.269517	3.896750
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C	4.273570	18.232132	2.820513	H	6.784537	14.720531	-0.598330
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C	5.462772	19.773841	4.356261	H	6.927646	15.606117	1.737806
C	5.920502	21.045935	4.690608	H	1.193767	-5.301269	2.032444
C	5.670755	22.136709	3.843509	H	1.706333	-7.697099	2.344289
C	4.952024	21.922878	2.655743	H	5.866634	-6.905739	1.491729
C	4.497516	20.649361	2.325942	H	5.340650	-4.516441	1.173558
H	5.664427	18.936719	5.025337	H	5.449857	-9.179775	1.912272
H	6.476433	21.189023	5.618582	H	5.586494	18.949134	5.036582
S	6.228133	23.799187	4.199033	H	6.393879	21.198085	5.651406
H	4.746941	22.758660	1.984968	H	4.755970	22.777711	1.979915
H	3.941731	20.498735	1.400137	H	3.956066	20.520755	1.373354
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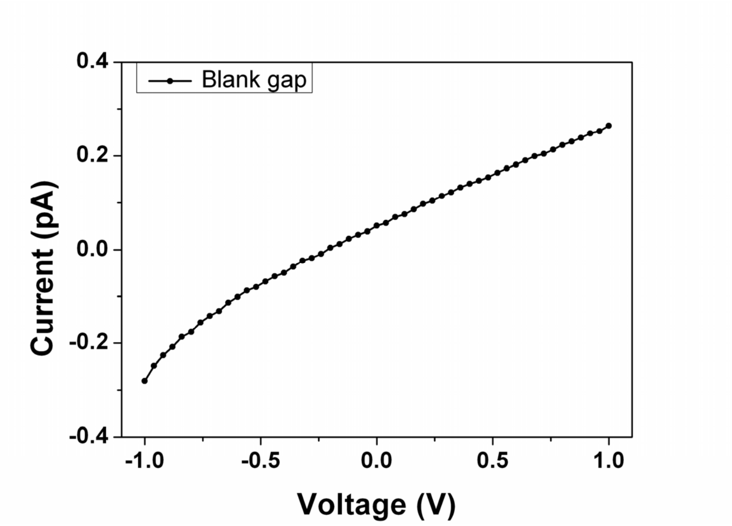

Figure S4. Representative *I-V* characteristics of blank ~3 nm OWL-generated gap device.

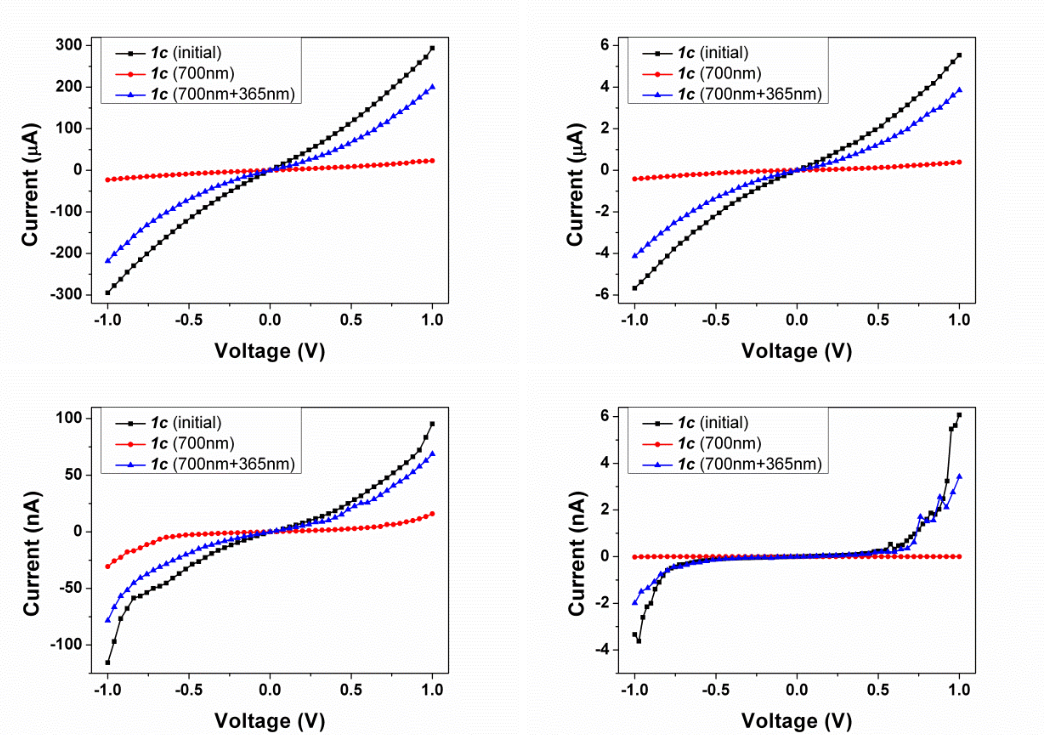

Figure S5. The *I-V* characteristics for different ~3 nm gap devices loaded with ***1c*** (measured in vacuum and dark).

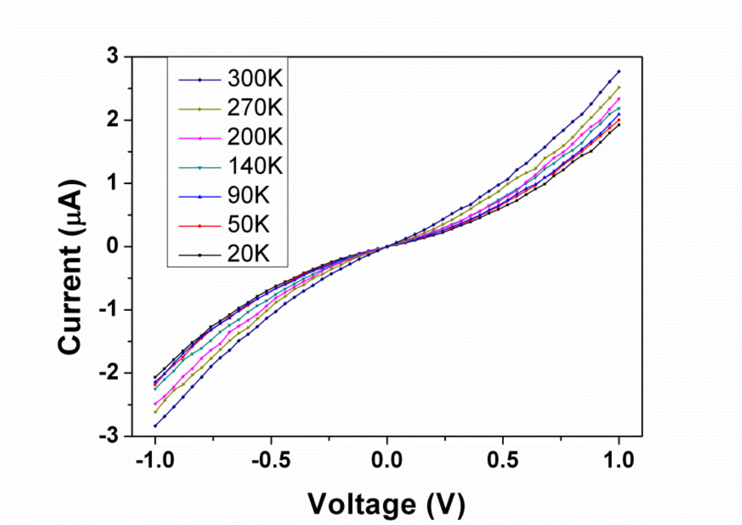

Figure S6. Temperature dependent *I-V* curves of 1c-modified ~3 nm nanogap device.

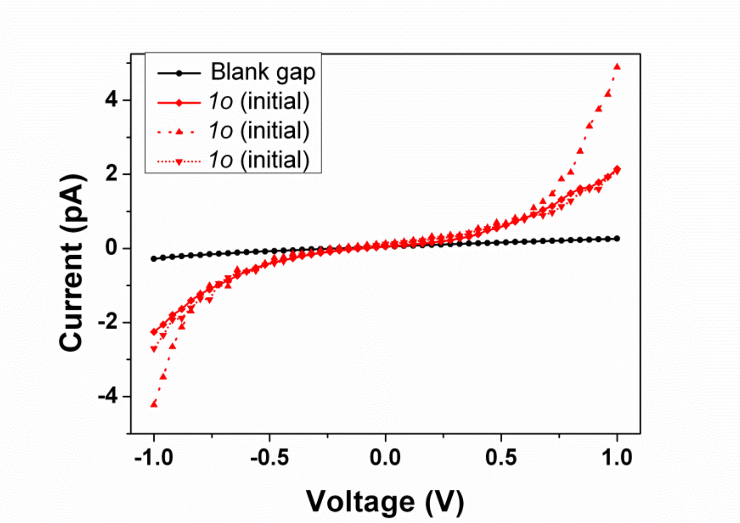

Figure S7. Representative *I-V* characteristics of blank (black curve) and different ***1o***-fabricated (red curves) ~3 nm OWL-generated gap devices.

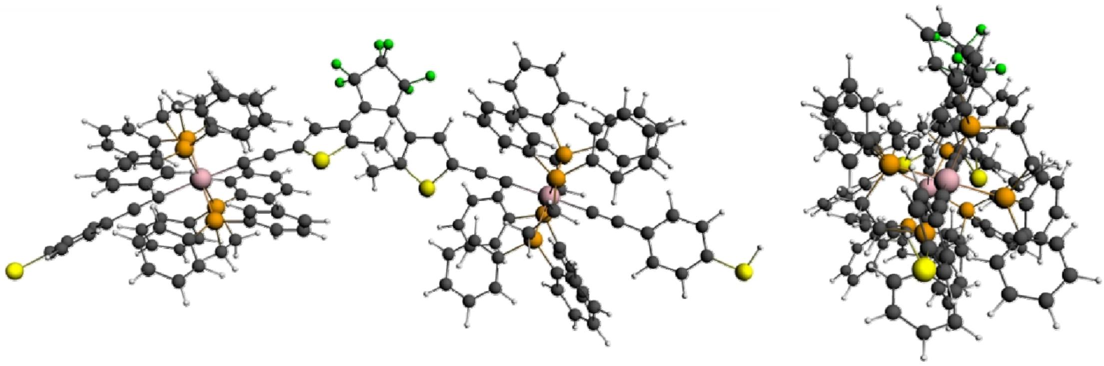

Figure S8. Side (left) and top (right) views of ***1o*** along the S-S axis obtained from the optimized simplified ***1o*** molecule by substituting hydrogen atoms of the dppe ligand by phenyl groups (no geometrical optimisation).

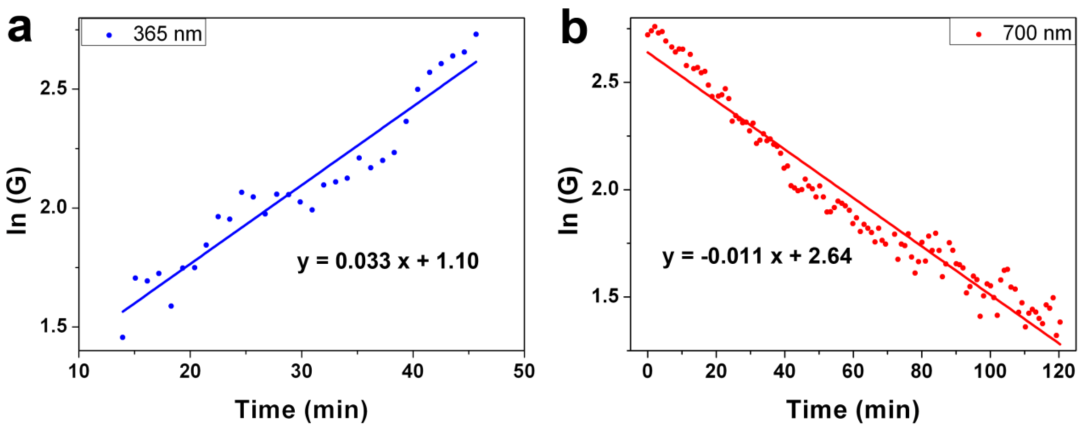

Figure S9. Plots of ln(G) vs time upon (a) 365 nm and (b) 700 nm irradiation. The slopes of the fitting lines reflect the reaction constant of the isomerization between ***1o*** and ***1c*** and vice versa.

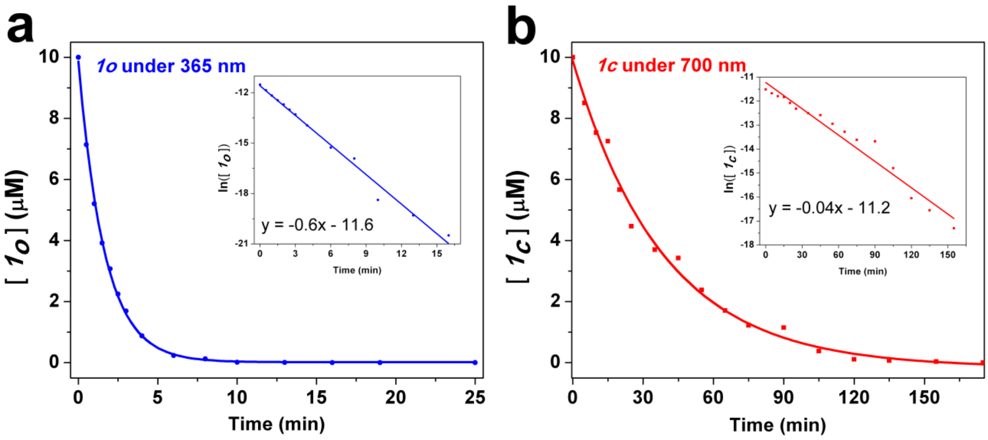

Figure S10. Plots of (a) ***1o*** concentration *vs* time upon 365 nm and (b) ***1c*** concentration *vs* time upon 700 nm irradiation in toluene. (The values of ***1*** concentration were calculated from the absorption values at 713 nm during irradiation and the initial concentration is 10 μM.) Inert: Plots of (a) ln(***1o*** concentration) *vs* time upon 365 nm and (b) ln(***1c*** concentration) *vs* time upon 700 nm irradiation. (The slopes of the fitting lines reflect the reaction constant of the isomerization between ***1o*** and ***1c*** and vice versa.)

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