Supporting Information

Pressure-Induced Conductivity in a Neutral Non-planar Spin-localized Radical

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1. Crystal data of radicals 1 and 2

Crystallographic measurements were carried out on a *BRUKER SMART APEX CCD* diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) from an x-Ray Tube. Programs used: data collection, Smart version 5.631 (Bruker AXS 1997-02); data reduction, Saint + version 6.36A (Bruker AXS 2001); absorption correction, SADABS version 2.10 (Bruker AXS 2001). Structure solution and refinement was done using SHELXTL Version 6.14 (Bruker AXS 2000-2003). Data collection, structure solution, refinement was performed by X. Fontrodona (Serveis Tècnics de Recerca, Universitat de Girona, Spain).

Red crystals of radical **2** (C₁₉ Cl₁₅) were grown from a slow diffusion of hexane in a CH₂Cl₂ solution of the compound, and used for room temperature (at 298(2) K) X-ray structure determination. The measurements were made in the range 1.469 to 28.285° for θ . Hemi-sphere data collection was carried out with ω and ϕ scans. A total of 19909 reflections were collected of which 14000 [R(int) = 0.0510] were unique.

The structure was solved by direct methods and refined by full-matrix least-squares methods on F². The non-hydrogen atoms were refined anisotropically. A considerable amount of spurious electron density non attributable to any solvent molecule was removed with the SQUEEZE option of PLATON.

Final R indices [I>2sigma(I)] **R1 = 0.0691**, wR2 = 0.1541

R indices (all data) R1 = 0.1766, wR2 = 0.2052

Dark crystals of radical dyad **1** (C₃₅ H₁₀ Cl₁₄ N S₄), were grown from hexane/dichlorometane, and used for room temperature (at 298(2) K) X-ray structure determination. The measurements were made in the range 2.040 to 28.354° for θ . Full-sphere data collection was carried out with ω and ϕ scans. A total of 64741 reflections were collected of which 20060 [R(int) = 0.1286] were unique.

The structure was solved by direct methods and refined by full-matrix least-squares methods on F². The non-hydrogen atoms were refined anisotropically. The H-atoms were placed in geometrically optimized positions and forced to ride on the atom to which they are attached.

Final R indices [I>2sigma(I)] **R1 = 0.0614**, wR2 = 0.1036

R indices (all data) R1 = 0.2193, wR2 = 0.1457

More information about the crystal structure of **1** is reported in reference S1.

Table S1. Crystal data and selected intermolecular distances for **1** and **2**.

	1	2
Formulas	$C_{35}H_{10}Cl_{14}NS_4$	$C_{19}Cl_{15}$
FW (g/mol)	1069.06	760.00
<i>a</i> (Å)	17.411(3)	8.960(3)
<i>b</i> (Å)	7.951(6)	13.051(5)
<i>c</i> (Å)	30.177(3)	27.917(10)
<i>V</i> (Å ³)	4060.98	3190.08
space group	<i>P</i> 2 ₁	<i>P</i> 1
Z	4	4
R-factor (%)	6.14	6.91
<i>ipso</i> -C-- <i>ipso</i> -C (Å)	7.952	13.05
<i>Ph</i> -C--- <i>Ph</i> -C planes (Å)	6.48 (7.952)	11.87 (13.05)

Figure S1. (a) ORTEP view of radical **2** at 300 K. (b) Asymmetric unit of radical **2**. Atoms are shown at the 50% probability level.

Figure S2. Molecular arrangement of radical **2** on the *bc* (left) and *ac* planes (right).

Figure S3. (a) ORTEP view of radical dyad **1** at 300 K. (b) Asymmetric unit of **1** on the *ac* plane. Hydrogen atoms are omitted for clarity. Atoms are shown at the 50% probability level.

Figure S4. Planes including the phenyl rings of the PTM unit of two adjacent molecules of radical dyad **1** on the *bc* plane.

Figure S5. Molecular arrangement of radical dyad **1** on the *ac* plane.

2. High-pressure conductivity measurements of radicals 1 and 2

High-pressure resistivity measurements of radicals **1** and **2** were carried out following the reported procedure by a diamond anvil cell (DAC) four-probe DC measurements.² Three single crystals of radical dyad **1** and three of radical **2** with average sizes of 0.11-0.13 mm were used for the high-pressure measurements. The four contacts were made by 10 μm (or 5 μm) gold wires and attached to the crystal with gold paint. The diamond culet size 0.7 mm and tension annealed SUS301 were used for the two first samples, and the diamond culet size 0.56 mm and Inconel 625 were used for the third sample, respectively. Daphne Oil 7373 was used as the pressure-transmitting medium. The pressure was determined by the shift of the ruby fluorescence R1 lines at room temperature.

Figure S6. Pictures of resistivity measurements of crystals (a) radical dyad **1** under 16.8 GPa, (b) radical **2** under 21.1 GPa.

Reversibility and reproducibility of conductivity measurements

(c)

Figure S7. Reversibility measurements on one sample of radical dyad **1** under (a) increasing pressure, (b) decreasing pressure and (c) pressure dependence of the conductivity σ (298 K) and of activation energy E_a (circle). The red symbols are increasing pressure data and the blue symbols are decrease pressure data.

Figure S8. Pressure dependence of the conductivity σ (298 K) (closed symbols) and E_a (open symbols) of three different crystals of radical dyad **1**.

Figure S9. Pressure and temperature dependence of the resistivity of sample #2 of radical dyad **1**.

3. Magnetic susceptibility of radical dyad 1

Figure S10. Magnetic susceptibility of crystals of radical dyad **1** as function of temperature.

4. Cyclic voltammetry of radicals 1 and 2

Figure S11. Cyclic voltammetry of solution of radical dyad **1** (above) and radical **2** (below) in CH_2Cl_2 vs. Ag/AgCl using $n\text{-Bu}_4\text{PF}_6$ (0.1 M) as electrolyte at 300 K under argon at a scan rate of 0.1 V/s. Ferrocene/ferrocinium (Fc/Fc^+) couple was used as internal reference.

5. Simulated crystal structures, band structures and charge transfer calculations of radical dyad 1 under pressure

We employed the projector augmented wave basis as implemented in VASP³ to predict the structure of **1** at elevated hydrostatic pressure. The calculations have been performed in two different ways: First as constant pressure predictions of the structure, using the Γ point only; then by constant volume calculations using a $2 \times 4 \times 2$ k mesh. Fig. S12 shows how lattice parameters a , b and c , monoclinic angle β and volume V evolve as function of hydrostatic pressure. The constant volume calculations yield lower enthalpies and are thus of higher quality (see Fig. S13). In Fig. S12, the constant pressure calculations are shown with dashed lines for comparison. Plane wave cutoff for the calculations shown here is 400 eV.

Figure S12. Simulation of the evolution of structural parameters of radical dyad **1** with hydrostatic pressure

Figure S13. Comparison of enthalpies as function of hydrostatic pressure for constant volume and for constant pressure simulations of radical dyad **1**.

Pressure (GPa)	Volume ($\text{\AA}^3/\text{molecule}$)	a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)	α ($^\circ$)	β ($^\circ$)	γ ($^\circ$)	Energy (Hartree/molecule)
-0.3	1050	17.907 ₃	7.9494	30.363 ₅	90	103.6619	90	- 9451.547208
0.13	1005	17.693 ₄	7.7440	30.161 ₂	90	103.4075	90	- 9451.533527
0.6	960	17.518 ₀	7.4985	30.003 ₃	90	103.0129	90	- 9451.514042
1.3	915	17.313 ₃	7.2453	29.891 ₀	90	102.5447	90	- 9451.486834
2.3	870	17.072 ₀	6.9768	29.878 ₉	90	102.0810	90	- 9451.449433
3.7	825	16.791 ₆	6.7062	29.914 ₇	90	101.5859	90	- 9451.398515
5.7	780	16.514 ₈	6.4492	29.855 ₀	90	101.1240	90	- 9451.328662
8.6	735	16.235 ₇	6.2001	29.716 ₂	90	100.6296	90	- 9451.232341
12.8	690	15.969	5.9566	29.480	90	100.1986	90	-

		8		3				9451.098249
18.9	645	15.704 2	5.7134	29.188 2	90	99.8841	90	9450.909632
27.8	600	15.422 9	5.4755	28.837 1	90	99.7591	90	- 9459.643142

Table S2. Pressure, cell parameters and energies of optimized crystal structures at different pressures.

Figure S14. Evolution of band structure and density of states of radical dyad **1** with hydrostatic pressure.

Figure S15. Wannier functions of radical dyad **1** around ambient pressure. **(a)** Wannier function for bands around E_F . **(b)** Wannier function for bands at $E = -0.15$ eV.

Figure S16. Wannier functions of radical dyad **1** at $P = 12.8$ GPa. **(a)** Wannier function for bands around E_F . **(b)** Wannier function for bands at $E = -0.25$ eV.

6. Experimental and simulated Raman spectra at ambient pressure of radical dyad 1

Raman measurements at high pressure were performed in a sapphire cell with a diameter culet of 360 μm and a gold gasket. No pressure transmitting medium was used and diamond chips were placed as the pressure calibrant. Raman measurements were performed using an air-cooled argon ion laser, a Spectra-Physics solid state laser, at 532.0 nm. Diamond chips were used as pressure sensor.⁴ The device is equipped with a 10x Mitutoyo long working distance objective coupled to a 10x Navitar zoom system and focused onto the slit of an ISA HR460 monochromator with a grating of 600 grooves mm^{-1} and a liquid nitrogen cooled CCD detector (ISA CCD3000, 1024–256 pixels). Spectra were measured with a spectral resolution of about 2–3 cm^{-1} and calibrated with a standard neon emission lamp. The SAC is mounted on a xyz stage, which allows us to move the sample with an accuracy of 1 μm . The typical sampling area was about 1–2 μm in diameter.

For all calculations the UM06 density functional theory was used⁵ in conjunction with the 6-31G** basis set.⁶ All computations were done with Gaussian 09.⁷ Reported frequencies are harmonic frequencies and were uniformly scaling throughout with the scaling factor of 0.96. The energy minimization of a single molecule was performed with starting geometry from the crystal structure. The minimum was confirmed by a vibrational frequency analysis: all computed frequencies were real. ChemCraf program was used for representing vibrational displacements.⁸ Spectra were generated by the GaussSum-2.2.5 program with a broadening of 3 cm^{-1} .⁹

Figure S17. Raman spectra at ambient pressure. (a) Experimental Raman spectrum of crystals of **1** measured at ambient pressure with a laser of 532 nm in the 1700–1450 cm^{-1} region. (b) Simulated Raman spectrum of **1** in the 1700–1450 cm^{-1} region.

Figure S18. Raman spectrum at ambient pressure. (a) Experimental Raman spectrum of crystal of **1** measured at ambient pressure with a laser of 532 nm in the 1450-800 cm^{-1} region. (b) Simulated Raman spectrum of **1** in the 1450-800 cm^{-1} region.

7. Raman bands assignments

Experimental Raman shift (cm ⁻¹)	Calculated Raman shift 0.96 scaled (cm ⁻¹)	Eigenvectors	Description
1618	1626		C-C stretching of vinylene + Inner phenyl C-C stretching
1597	1593		+ Inner phenyl C-C stretching + C-C stretching of vinylene
1573	1568		C=C stretching of the TTF
1515	1537		C=C stretching of the TTF + C=C stretching of the pyrrol
1501	1491		Anti-symmetric C=C stretching of the inner PTM
1486	1480		PTM anti-symmetric C=C stretching
1311	1290		Pyrrol breathing + Phenyl breathing + in plane CH bending
1256	1230		PTM breathing + in plane CH bending
1205	1169		Pirrol breathing + in plane CH bending
1182	1160		In plane CH bending + phenyl breathing + pirrol breathing + PTM stretching
967	965		Vynil's CH out of plane bending
939	912		Pyrrol breathing + phenyl breathing
887	843		Phenyl CH Out of plane bending

Figure S19. Vibrational eigenvectors associated with the most relevant bands of the Raman spectrum of 1 dye. Values obtained from calculations with UM06/6-31G(d,p) followed by uniform frequency scaling with a value equals to 0.96.

8. Experimental and simulated Raman spectra of radical dyad 1 at different pressures

For all calculations the UM06 density functional theory was used in conjunction with the 6-31G** basis set.⁶ All computations were done with Gaussian 09.⁸ Reported frequencies are harmonic frequencies and were uniformly scaling throughout with the scaling factor of 0.96.⁷ A single molecule from the predicted crystal structure was performed with starting geometry from the crystal structure optimization at each pressure with full potential local orbital (FPLO) basis set and GGA functional. Spectra were generated by the GaussSum-2.2.5 program with a broadening of 3 cm⁻¹.

Figure S20. (a) Experimental and (b) UMO6/6-31G** simulated Raman spectrum of crystal of radical dyad 1 in the 1800-800 cm⁻¹ region at different pressures.

Figure S21 Raman shift pressure evolution of the dyad **1**. Pink symbols correspond to the PTM anti-symmetric C=C stretching modes; blue symbols to the C=C stretching of the TTF modes and red symbols to the C-C stretching of vinylene + Inner phenyl C-C stretching mode. Open and closed symbols are used to distinguish between the two different contributions of each kind of vibrational mode. Experimental data have been fitted to a triple linear trend; solid lines correspond to such fit. Vertical grey regions correspond to the pressures of interception between each linear trend.

Table S3. Experimental interceptions and pressure coefficients of the dye **1** Raman bands before in the first, second and third regimens, S_1 , S_2 and S_3 , respectively

	PTM anti-symmetric C=C stretching		C=C stretching of the TTF		C-C stretching of vinylene + Inner phenyl C-C stretching	
ω_0 (cm ⁻¹)	1488	1501	1515	1573	1597	1618
S_1 (cm ⁻¹ /GPa)	0±0	2±1	3±1	4±2	1.1±1.0	0.4±1.0
S_2 (cm ⁻¹ /GPa)	4.6±0.6	5.7±0.6	6.9±0.6	1.8±0.8	3.1±0.5	2.5±0.5
S_3 (cm ⁻¹ /GPa)	1.6±0.5	2.7±0.5	3.5±0.5	2.6±0.5	2.0±0.5	3.1±0.5

Figure S22. Pressure dependent data obtained from the calculated M06/6-31G** Raman spectra
a) Intensity ratio of Raman bands of radical dyad **1** assigned to: C=C stretching of TTF+PTM/vinylene. b) Raman shift pressure evolution of the dyad **1**. Pink symbols correspond to the PTM anti-symmetric C=C stretching modes; blue symbols to the C=C stretching of the TTF modes and red symbols to the C-C stretching of vinylene + Inner phenyl C-C stretching mode. Data have been fitted to a double linear trend; solid lines correspond to such fit. Vertical grey regions correspond to the pressures of interception between each linear trend

Table S4. Calculated UM06/6-31G** interceptions and pressure coefficients of the dye 1 Raman bands before in the second and third regimens, S_2 and S_3 , respectively. There is no first regimen since experimentally it is assigned to changes in molecular packing and for Raman calculations we are taking into account a single molecule.

	PTM anti-symmetric C=C stretching	C=C stretching of the TTF		C-C stretching of vinylene + Inner phenyl C-C stretching
ω_0 (cm^{-1})	1470	1491	1530	1580
$S_2(\text{cm}^{-1}/\text{GPa})$	4.6 ± 0.3	1.8 ± 0.2	1.6 ± 0.2	2.4 ± 0.2
$S_3(\text{cm}^{-1}/\text{GPa})$	2.0 ± 0.1	2.5 ± 0.1	2.3 ± 0.1	1.7 ± 0.1

Experimentally it is observe that all the analyzed bands shift in there different regimens: 0- (2.5 ± 0.5) GPa; $-(2.5 \pm 0.5)$ - $-(8 \pm 1)$, and $-(8 \pm 1)$ to the upper limit. This fittings have been done with a triple linear fit in which the transitions points are shared between all the data. The Raman shift in the first regimen is significantly lower than in the second one. This is because in this first low pressure range molecular changes related with crystal rearranges occur and these do not induce large intra molecular effects. Thus it can be said that it is in the second regimen when pressure induces intramolecular effects which alter C-C distances. It is seen that pressure coefficients of the terminal units are larger than those of the central vinylene unit, in agreement with a structural and electronic reorganization towards this central unit. Additionally, these experimental values are in good agreement with those theoretically calculated: larger coefficients in the terminal units. However, in the single molecule high pressure dependent calculated spectra the first regimen which confirms that experimentally mainly inter molecular reorganization occurs. Because of the Raman computations on the high pressure molecules are done without energy minimization on a single molecule taken from the optimized crystal, these Raman spectra do show imaginary frequencies and also not all the bands are observed. Nevertheless, the pressure transition at 8 GPa would correspond with that predicted at around 6 GPa from the calculated Raman spectra.

On the other hand, this high pressure behavior is uniquely observed to this molecular system. High pressure studies reported in the literature on analogues systems gathered Raman shift linear trends with lower pressure coefficients.⁹

Figure S23. Three individual Raman experiments at pressures of a) 1.6 GPa, b) 6.0 GPa, c) 14.5 GPa. Black line from below shows the initial Raman at ambient pressure, pink line the spectrum at the highest pressure reached in that experiment, and orange line is the spectrum after applying the pressure outside the cell.

9. High-pressure photoluminescence measurements

Two different high pressure experiments were conducted in a sapphire anvil cell (Figure S24)^{4,11}. The pristine sample was used as starting material which was placed on a non-drilled gold gasket in the same conditions. In the experiments diamond chips were placed as the pressure calibrant and anvils had culets of with a 380 μm . Raman and photoluminescence measurements were performed using an air-cooled argon ion laser, a Spectra-Physics solid state laser, operating at 532.0, nm.

Figure S24. Deconvolution of the high resolution photoluminescence spectra of crystals of radical dyad **1** at selected pressures when the sample was monochromatically excited with 532 nm. The experiments were conducted with a sapphire anvil cell. In green a low wavelength band have been fitted and in black the growing high wavelength band, assigned to the intermolecular charge transfer. Red line corresponds to the sum of both contributions.

In Figure S24 it can be seen that parallel to the intensity growth of the band assigned to the SOMO-LUMO transition, 680 nm, another feature appears at slightly higher energy (1.9 eV). The intensity of the latter is lower than that of the band at 680 nm. However, when the photoluminescence spectrum of the sample out of the anvil was measured (Figure S26) none of these bands were visible. We speculate about the possibility that the high energy band sets its origin in an analogous intermolecular charge transfer transitions.

Figure S25. Pressure evolution of: a) wavelength of the bands, b) intensity ratio of the 680 nm band divided by the intensity of the 630 nm band.

In Figure S25a we have represented the wavelength of both contributions as a function of pressure. It seems like there is a slight upshift with increasing pressure in both bands. Additionally in Figure S25b the relative area of the 680 nm band respect the 630 nm band is represented as a function of pressure. It is seen how the intensity of the band at 680 nm rapidly increases with pressure.

In Figure S26 the photoluminescence spectrum of the recovered sample after pressure cycle is represented together with the spectrum of the pristine sample. It is seen that in the recovered sample both of the contributions remain but that around 1.8 eV has strongly increased in intensity.

Figure S26. Photoluminescence spectra when the sample was excited at 532 nm of crystals of radical dyad **1** at room pressure before (black line) and after pressure (orange line) treatment (a) up to 6 GPa and (b) up to 12 GPa.

Table S5. Extracted results of DFT calculations (UM06/6-31G**) (264A is SOMO). Orbital energies in Hartrees.

P (GPa)	Absorption wavelength (nm)	Oscillator strength	Main transition involved	
0	522.61 nm	f=0.1885	264A ->266A	0.54855
1	524.66 nm	f=0.1844	264A ->266A	0.55246
2	527.05 nm	f=0.1790	264A ->266A	0.55221
3	529.35 nm	f=0.1690	264A ->266A	0.54782
4	532.85 nm	f=0.1653	264A ->266A	0.54648
5				
6	538.15 nm	f=0.1779	264A ->266A	0.54336
7	539.12 nm	f=0.1846	264A ->266A	0.55816
8	539.54 nm	f=0.2044	264A ->266A	0.56917
9	539.95 nm	f=0.1987	264A ->266A	0.57295
11	539.19 nm	f=0.1767	264A ->266A	0.57176
13	537.67 nm	f=0.1507	264A ->266A	0.56447
15	535.98 nm	f=0.1250	264A ->266A	0.55425
16	534.80 nm	f=0.1106	264A ->266A	0.54843
17	559.18 nm	f=0.3355	264B ->266B	0.88149
20	544.74 nm	f=0.4052	264B ->266B	0.86930

0GPa

270 (a)		-0.03797	270 (a)		-0.03341
269 (a)		-0.04455	269 (a)		-0.03962
268 (a)		-0.05249	268 (a)		-0.04850
267 (a)		-0.05862	267 (a)		-0.05458
266 (a)		-0.08403	266 (a)		-0.08017
265 (a)		-0.17275	265 (a)		-0.13576
264 (a)		-0.21171	264 (a)		-0.17281
263 (a)		-0.22912	263 (a)		-0.22803
262 (a)		-0.23382	262 (a)		-0.22952

6GPa

266

265

264

263

270 (a)		-0.03746	270 (a)		-0.03340
269 (a)		-0.04282	269 (a)		-0.03740
268 (a)		-0.05171	268 (a)		-0.04769
267 (a)		-0.05634	267 (a)		-0.05169
266 (a)		-0.08264	266 (a)		-0.07869
265 (a)		-0.17153	265 (a)		-0.13594
264 (a)		-0.20961	264 (a)		-0.17155
263 (a)		-0.22899	263 (a)		-0.22700
262 (a)		-0.23261	262 (a)		-0.22952

11GPa

266

265

264

263

Figure S27. Selected frontier orbitals of dyad **1** calculated at 0, 6 and 11 GPa.

10. Evolution of magnetic moment and spin density of **1** with pressure

The evolution of the magnetic moment in all radical dyad **1** (and for the MPTTF unit) was estimated from crystalline calculations observing that it changes only slightly with pressure. Indeed, the total magnetic moment of the dyad is reduced under pressure when the material becomes metallic in the calculations. MPTTF contribution is small (0.1 – 0.2) and even slightly decreased with the pressure.

Figure S28. Evolution of the total magnetic moment (μ_B) of radical dyad **1** and for the MPTTF unit when increasing the pressure.

The spin density for a single molecule was calculated for comparison purpose. The geometry of the molecules was taken from the optimized crystal structures at different pressures within density functional theory calculations by performing relaxations of lattice parameters, monoclinic angle and internal atom positions at constant volume with the VASP code. Then over the taken molecular geometry for each pressure DFT single point calculations on at the UMo6/6-31G(d,p) level were conducted with Gaussian 09. The corresponding results are represented in Figure S29, where we have divided the molecule in several sections, as done along the manuscript. Initially at 0 GPa, the 94% spin density is located in the center C of the PTM radical. This radical character of the PTM remains with the increasing pressure and there is a minor decrease of the radical character in the PTM to 92%, which occurs by its proportional increase in the bridge and TTF units, 2% and 6% of radical character, respectively. Thus, we can see that although the spin density is mainly localized on the PTM moiety is slightly delocalized over the rest of the molecule.

Figure S29. a) Valence bond representation of the a single molecule taken from the optimized crystal structures of **1** at different pressures within density functional theory calculations by performing relaxations of lattice parameters, monoclinic angle and internal atom positions at constant volume with the VASP code. Spin density as function pressure, for a single molecule is calculated at the UMo6/6-31G(d,p) level. b) Image of per-atom spin density, at 0 GPa and 11 GPa, the bottom chart corresponds to the color scale representing the spin density distribution. c) Spin density calculated for a single molecule of **1** at the UMo6/6-31G(d,p) level divided for the different molecular sections.

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