

Electronic Supporting Information

Ionic couple-driven palladium leaching by organic triiodide solutions

Mariangela Cuscusa, Americo Rigoldi, Flavia Artizzu, Roberto Cammi, Paolo Fornasiero, Paola Deplano, Luciano Marchiò,* and Angela Serpe*

Including pages S1 – S18

Figures S1 – S11

Tables S1 – S4

Schemes S1 – S2

Refs S1

X-Ray molecular structure of the (PhHN)₂DTLI_n salts

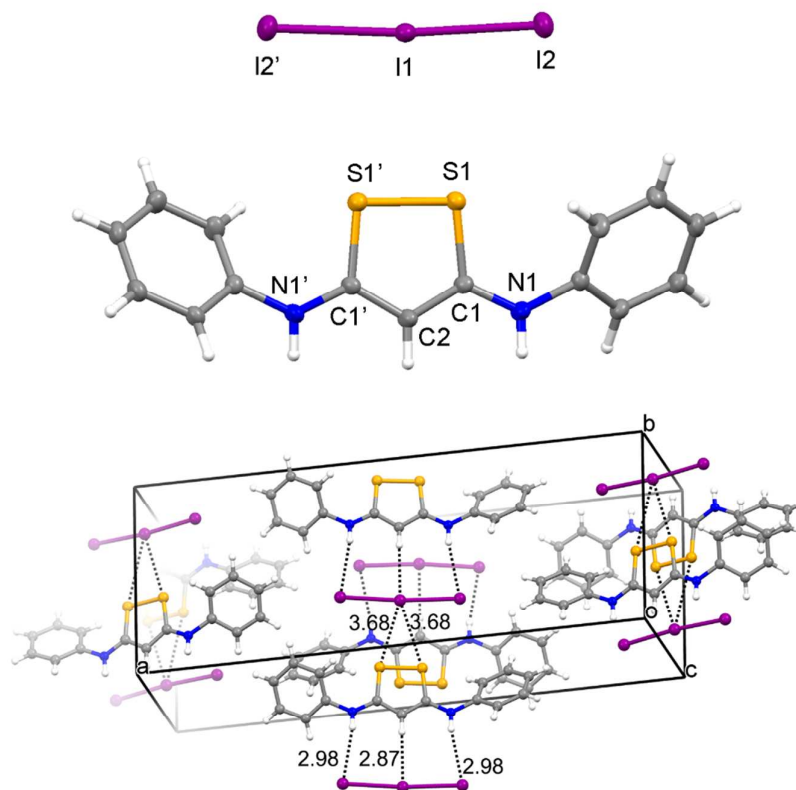


Figure S1. Molecular structure (above) and crystal packing (below) of (PhHN)₂DTLI₃. Weak interactions are represented as dashed lines. Symmetry code ' = -x; y; ½-z. The molecular structure of (PhHN)₂DTLI₃ shows remarkable similarities with that of **5**, Figure S5. The I₃⁻ exchanges three types of interactions with the cation.

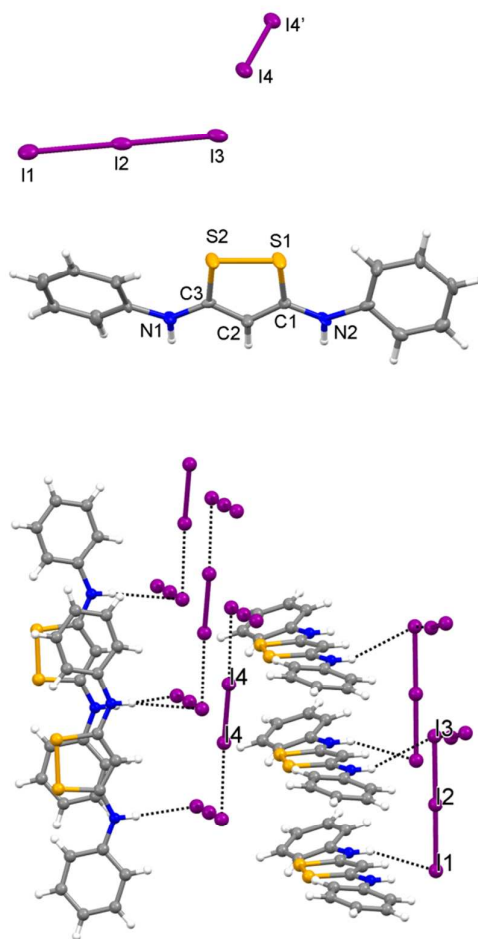


Figure S2. Molecular structure (above) and portion of the crystal packing (below) of $(\text{PhHN})_2\text{DTLI}_5$. Weak interactions are represented as dashed lines. The linear I_3^- anion bridges between two cations with the terminal iodine atoms and by interacting with two NH groups. The I_2 is interposed between two symmetry related I_3^- anions.

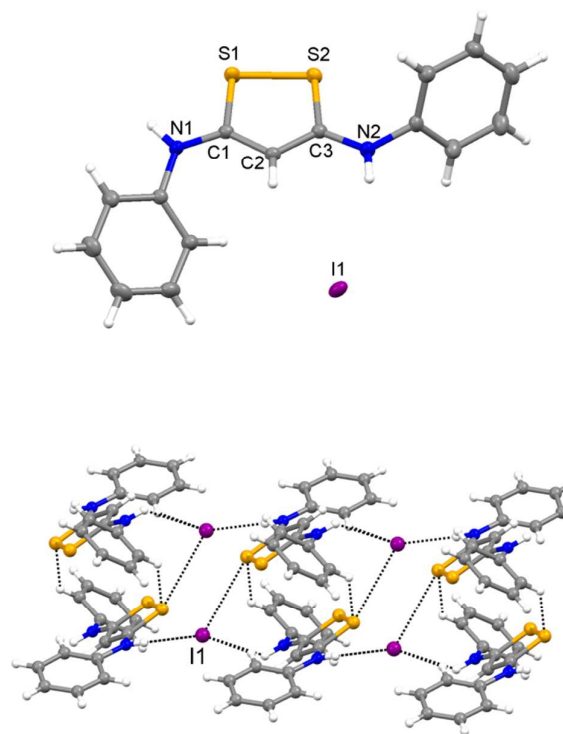


Figure S3. Molecular structure (above) and portion of the crystal packing (below) of (PhHN)₂DTLI. Weak interactions are represented as dashed lines.

X-ray molecular structures of the ionic couples

2 crystallizes in two different polymorphs (form A and form B), which mainly differ by the mutual orientation of the Mo₂DTL⁺ cation and the [Pd₂I₆]²⁻ complex anion. In form A, the angle between the planar anionic moiety and the planar C₃S₂ core is approximately 26°, whereas in form B, the same angle is approximately 73°. In both systems the S(1)-S(2) fragments interacts with the peripheral iodine atom, I(1), and with the bridging iodine atom, I(2), in a side-to-side orientation.

The bond distances within the N₂C₃S₂ fragment are consistent with the presence of a single bond between the S-S and C-S groups and with partial double bond character in the N-C-C-N system. The two morpholino residues adopt a chair conformation in both compounds, but a comparison between the two Mo₂DTL⁺ fragments reveals that the peripheral fragments are not superimposable for the two structures. The [Pd₂I₆]²⁻ system exhibits nearly the same geometric parameters in both forms. The metals have a square-planar geometry, which is slightly distorted since Pd-I(2)-Pd angle is significantly greater than 90° whereas the I(2)-Pd-I(2) angle is significantly smaller than 90°. The crystal packing of the two forms is also markedly different, Figure S4.

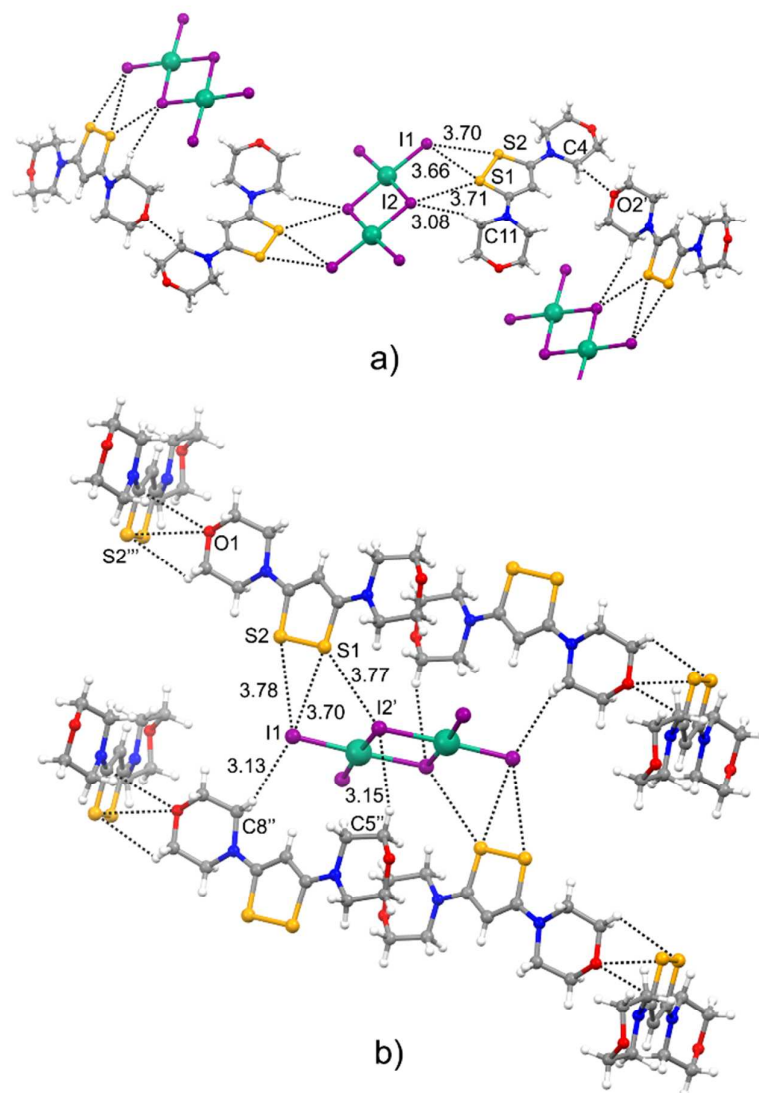


Figure S4. a) Portion of the crystal packing of $(\text{Mo}_2\text{DTL})_2[\text{Pd}_2\text{I}_6]$ (**2**) form A. Symmetry code ' = $\frac{1}{2}-x$; $-\frac{1}{2}+y$; $\frac{3}{2}-z$. b) Portion of the crystal packing of $(\text{Mo}_2\text{DTL})_2[\text{Pd}_2\text{I}_6]$ (**2**) form B. Symmetry codes ' = $-x$; $1-y$; $-z$, '' = $x-1$; y ; z , ''' = $\frac{1}{2}+x$; $\frac{3}{2}-y$; $\frac{1}{2}+z$. Weak interactions are represented as dashed lines and expressed in Å

The molecular structure of **5** shows that the $(\text{PhHN})_2\text{DTL}^+$ cation exchanges three types of interactions with the almost linear $[\text{AuI}_2]^-$ anion. Interestingly, the distance between nitrogen atoms of the cation (4.79 Å) is close to the distance between the iodine atoms of the anion (5.32 Å). This factor, together with the planarity of the N_2C_3 system, implies that two strong $\text{N-H}\cdots\text{I}$ interactions can be formed ($d(\text{N}\cdots\text{I}) = 3.768(8)$ Å). Moreover, the central C-H group is close to the metal ($d(\text{C}\cdots\text{Au}) = 3.73(1)$ Å) but the interaction seems weaker than the $\text{N-H}\cdots\text{I}$ ones. In fact, the $[\text{AuI}_2]^-$ fragment deviates from linearity ($\sim 176^\circ$) and this may be a consequence of the different strength of the interactions exchanged between anion and cation. The crystal packing of **5**, Figure S5, shows the presence of strongly interacting ionic couples that are stacked in a head-to-tail fashion (the metal lies over the central C-H group) and with the peripherals aromatic moieties that are facing each other.

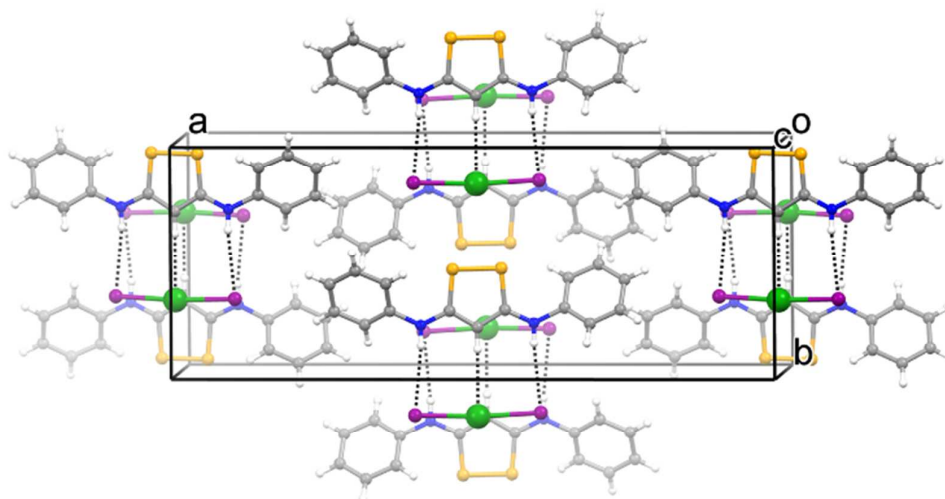


Figure S5. Crystal packing of $[(\text{PhHN})_2\text{DTL}][\text{AuI}_2]$ (**5**) viewed along the c axis. Weak interactions are represented as dashed lines.

The molecular structure of **6** comprises two different $[\text{AuI}_2]^-$ fragments that differently interact with the Mo_2DTL^+ cation. In one of them, each of the two iodine atoms of the linear $\text{I}(1)\text{-Au}(1)\text{-I}(1)$ moiety exchange a moderately strong interaction with one of the morpholino C-H ($d(\text{C}\cdots\text{I}) = 3.87(1)$ Å). The other one is located into a channel-like cavity and is severely disordered in various positions. For some molecules, interactions between the sulfur atoms of the cation and the iodine atoms of the anion are observed, Figure S6.

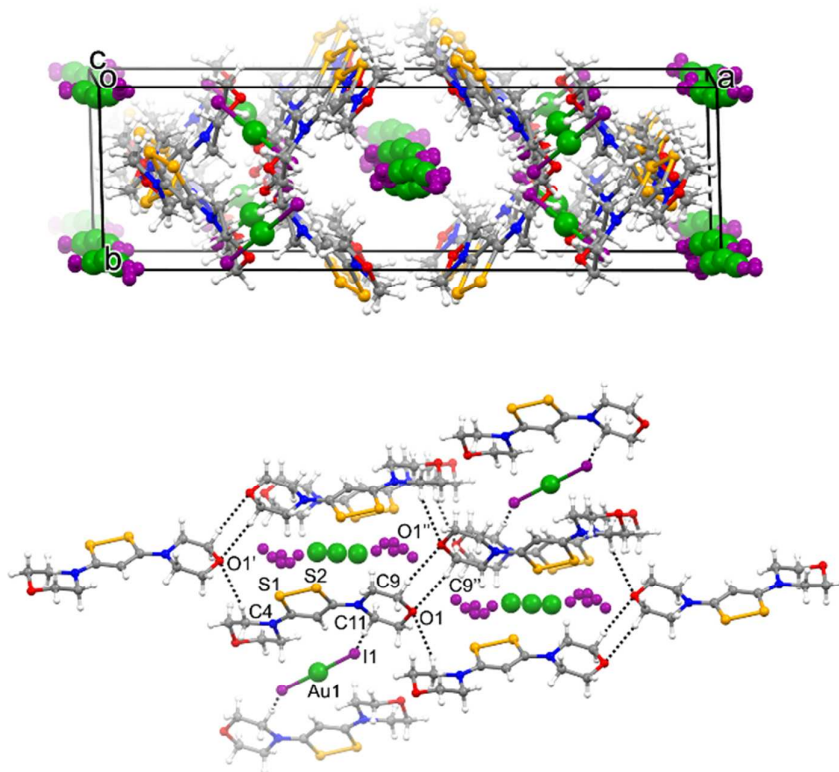


Figure S6. Above, crystal packing of $(\text{Mo}_2\text{DTL})[\text{AuI}_2]$. Below, interactions exchanged by the molecular fragments. Symmetry codes ' = $x; 1-y; -1/2+z$; '' = $-x; 1-y; 1-z$. Weak interactions are represented as dashed lines.

Table S1. Summary of X-ray crystallographic data for (Mo₂DTL)₂[Pd₂I₆] (**2**) form A, (Mo₂DTL)₂[Pd₂I₆] (**2**) form B, [(PhHN)₂DTL][AuI₂] (**5**), and (Mo₂DTL)[AuI₂] (**6**).

Empirical	C ₂₂ H ₃₄ I ₆ N ₄ O ₄ Pd ₂ S	C ₂₂ H ₃₄ I ₆ N ₄ O ₄ Pd ₂ S	C ₁₅ H ₁₃ AuI ₂ N ₂ S ₂	C ₁₁ H ₁₇ AuI ₂ N ₂ O ₂ S ₂
Formula weight	1590.97	1590.97	736.16	724.15
Colour, habit	Black, <u>needle</u>	Black, <u>prism</u>	Brown, block	Black, <u>needle</u>
Crystal size,	0.16x0.04x0.04	0.16x0.15x0.10	0.46x0.38x0.38	0.23x0.21x0.08
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /n	<i>P</i> bcn	<i>C</i> 2/c
<i>a</i> , Å	8.838(3)	10.537(1)	25.306(4)	33.335(4)
<i>b</i> , Å	12.593(5)	19.616(2)	9.722(1)	7.465(1)
<i>c</i> , Å	17.287(6)	10.653(1)	7.781(1)	20.567(3)
α , deg.	90	90	90	90
β , deg.	90.574(7)	116.131(1)	90	127.212(2)
γ , deg.	90	90	90	90
<i>V</i> , Å ³	1924(1)	1976.9(3)	1914.3(4)	3831.4(9)
<i>Z</i>	2	2	4	8
<i>T</i> , K	293(2)	293(2)	293(2)	293(2)
ρ (calc), Mg/m ³	2.626	2.555	2.554	2.511
μ , mm ⁻¹	5.999	5.839	11.125	11.122
θ range, deg.	2.00 to 26.46	2.08 to 27.30	1.61 to 25.77	1.63 to 24.77
No. of rflcn/uniq	22964 / 3954	25478 / 4451	9068 / 1818	7457 / 3262
GooF	1.007	1.035	1.008	1.031
<i>R</i> 1	0.0326	0.0256	0.0541	0.0543
<i>wR</i> 2	0.0644	0.0591	0.1528	0.1521

Table S2. Summary of X-ray crystallographic data for (PhHN)₂DTLI₃, (PhHN)₂DTLI₅, and (PhHN)₂DTLI.

Empirical formula	C ₁₅ H ₁₃ I ₃ N ₂ S ₂	C ₁₅ H ₁₃ I ₄ N ₂ S ₂	C ₁₅ H ₁₃ IN ₂ S ₂
Formula weight	666.09	792.99	412.29
Colour, habit	Orange, block	Orange, needle	Yellow, prism
Crystal size, mm ³	0.45 x 0.38 x 0.38	0.31 x 0.04 x 0.04	0.36 x 0.19 x 0.11
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	<i>Pbcn</i>	<i>P2₁/a</i>	<i>P</i> -1
a, Å	25.402(3)	18.217(4)	a = 8.873(1) Å
b, Å	9.768(1)	5.297(1)	b = 9.490(1) Å
c, Å	7.834(1)	21.885(5)	c = 10.518(1) Å
α, deg.	90	90	91.042(2)
β, deg.	90	92.935(4)	93.279(2)
γ, deg.	90	90	115.946(2)
Volume, Å ³	1943.8(4)	2109.0(8)	794.17(14)
Z	4	4	2
T, K	293(2) K	293(2) K	293(2) K
ρ (calc), Mg/m ³	2.276	2.497	1.724
μ, mm ⁻¹	5.036	6.108	2.270
θ range, deg.	1.60 to 26.10.	0.93 to 23.89.	1.94 to 27.32
No. of rflcn/uniq collected	9054/1925	9782/3230	10327/3567
GooF	1.005	1.003	1.009
R1 [I>2sigma(I)]	0.0325	0.0557	0.0213
wR2	0.0779	0.0887	0.0532

DFT optimization of $[(\text{PhHN})_2\text{DTL}]^+ / [\text{Pd}_2\text{I}_6]^{2-}$ ionic couple geometries.

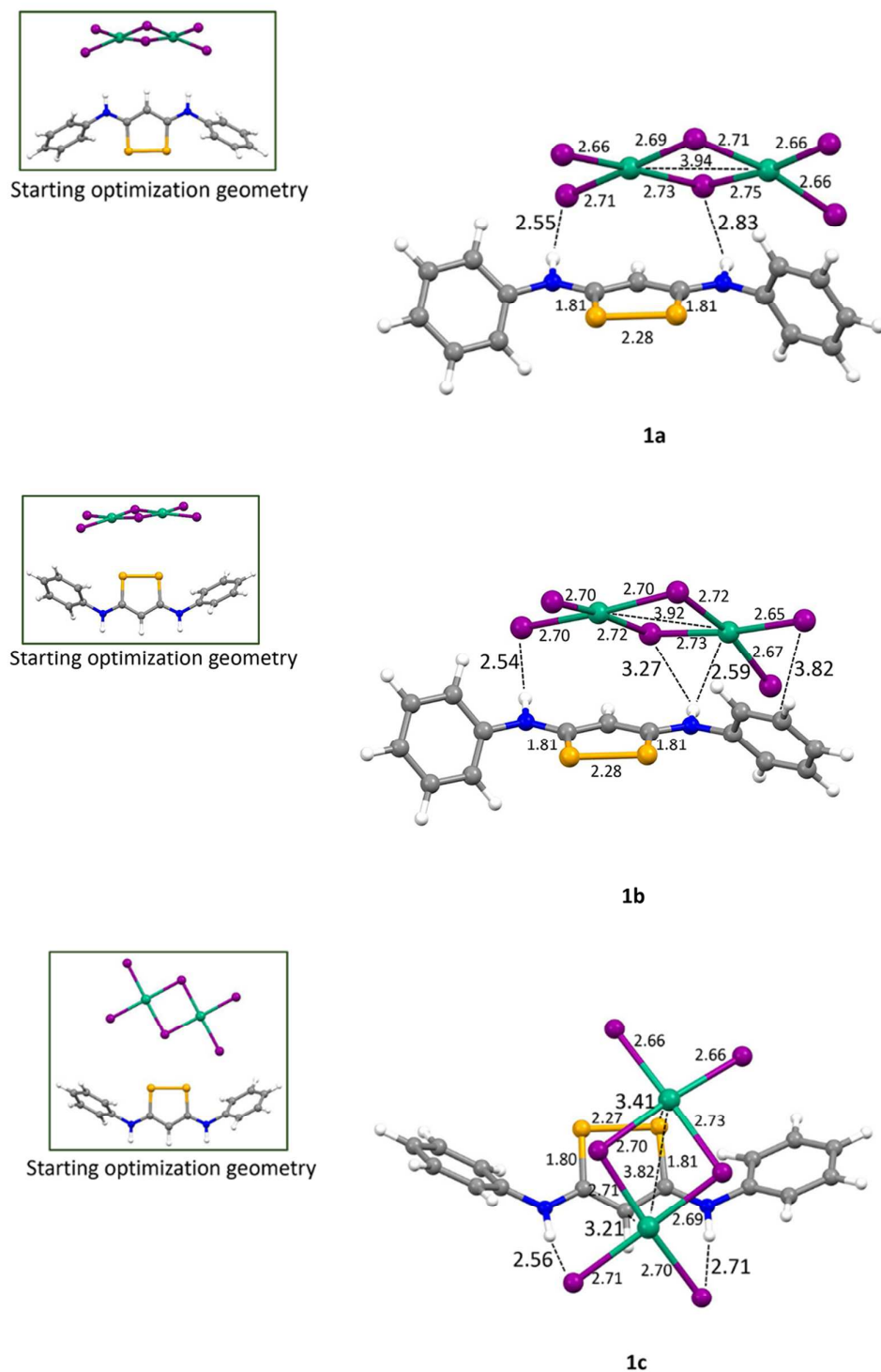


Figure S7. Optimized geometries of **1a**, **1b** and **1c** ionic couples. Distances are reported in Å. M05-2X density functional. SDD basis set. Pd and I were treated with MWB28 and MWB46 pseudopotentials, respectively.

Hirshfeld surface analysis of 2A, 2B, 3 and 4.

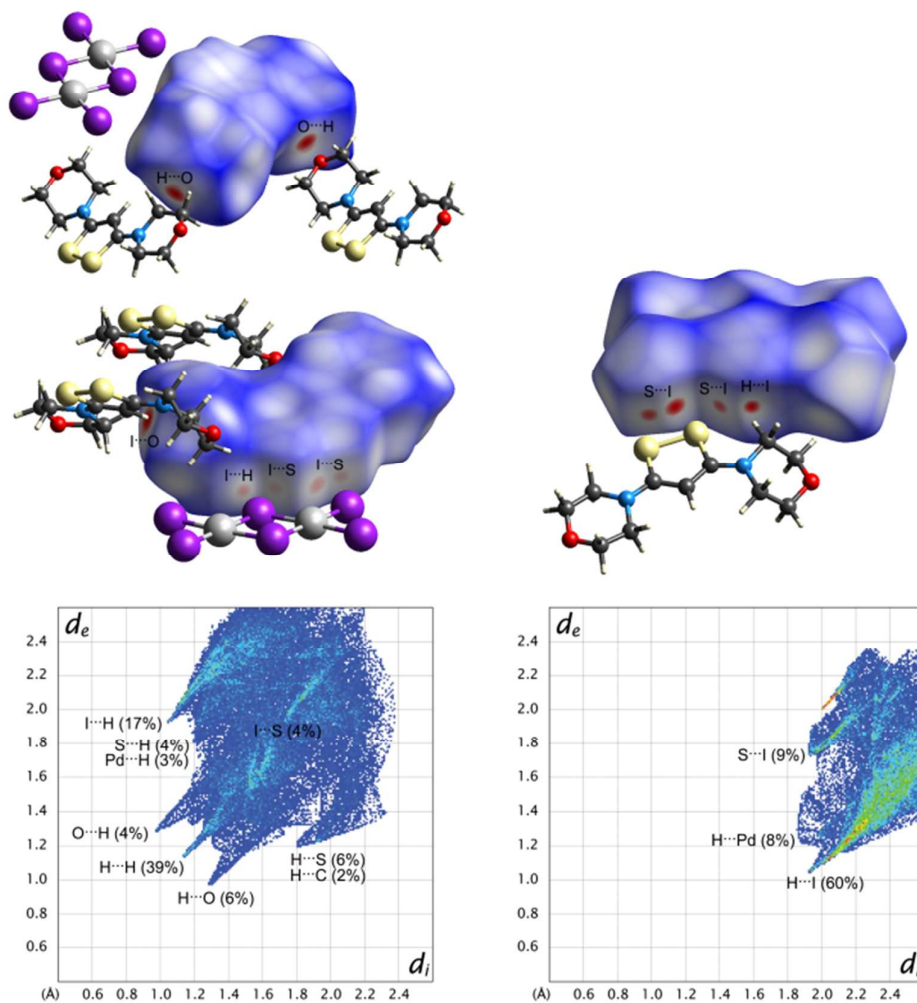


Figure S8. Hirshfeld surface (HS) and fingerprint plots of the form A of $(\text{Mo}_2\text{DTL})_2[\text{Pd}_2\text{I}_6]$ (2). Left, cation Mo_2DTL^+ ; right, anion $[\text{Pd}_2\text{I}_6]^{2-}$.

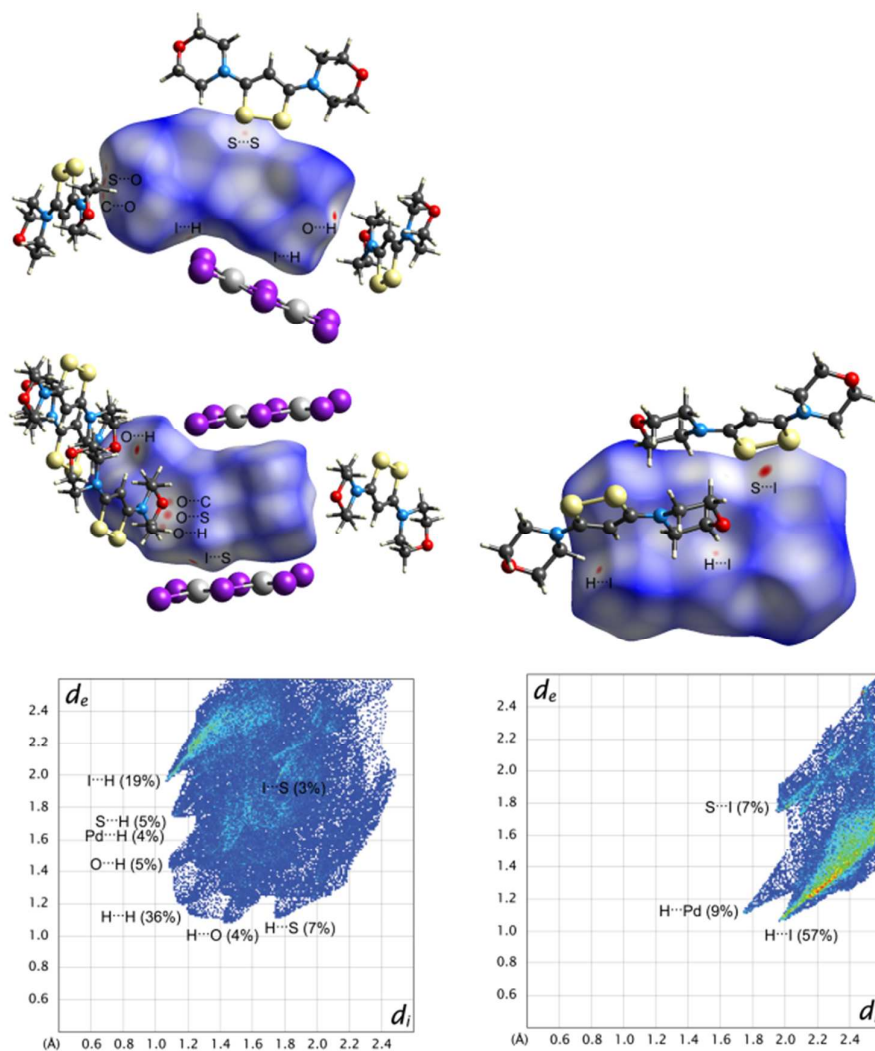


Figure S9. Hirshfeld surface (HS) and fingerprint plots of the form B of $(\text{Mo}_2\text{DTL})_2[\text{Pd}_2\text{I}_6]$ (2). Left, cation Mo_2DTL^+ ; right, anion $[\text{Pd}_2\text{I}_6]^{2-}$.

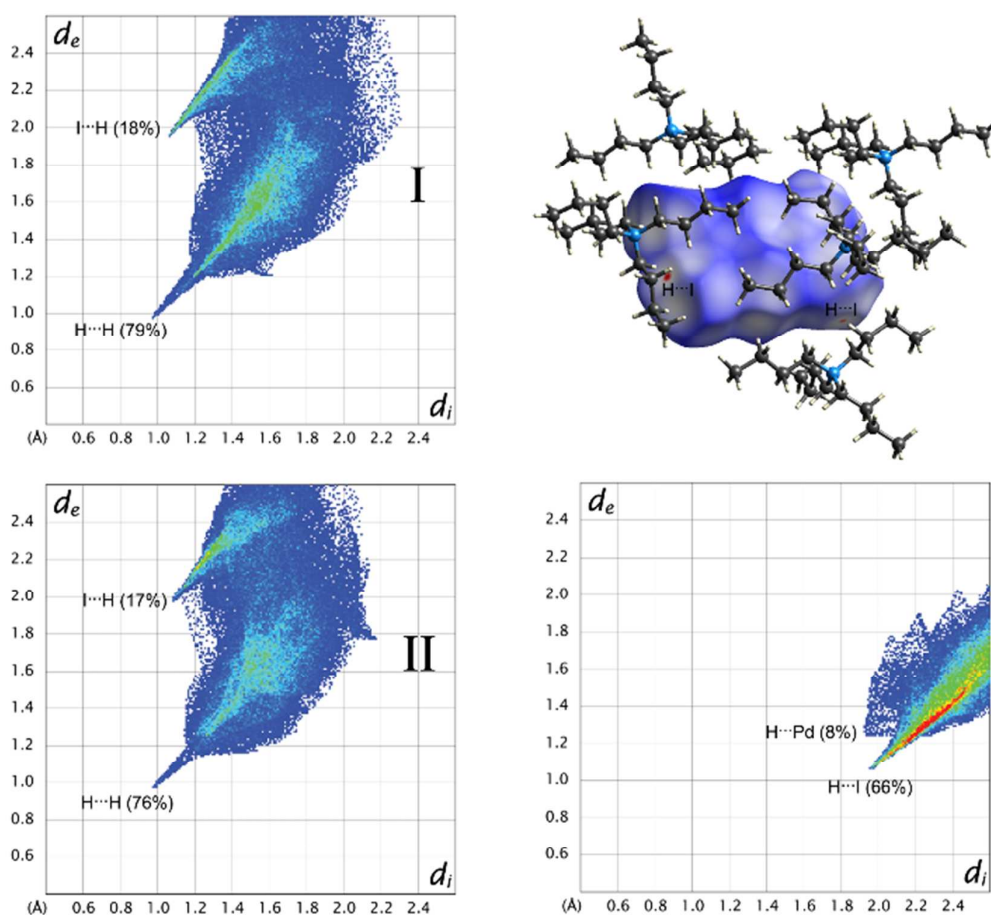


Figure S10. Hirshfeld surface (HS) and fingerprint plots of $(\text{TBA})_2[\text{Pd}_2\text{I}_6]$ (**3**). Left, fingerprint plots of the two independent TBA cations of the asymmetric unit (I and II); bottom right, anion $[\text{Pd}_2\text{I}_6]^{2-}$.

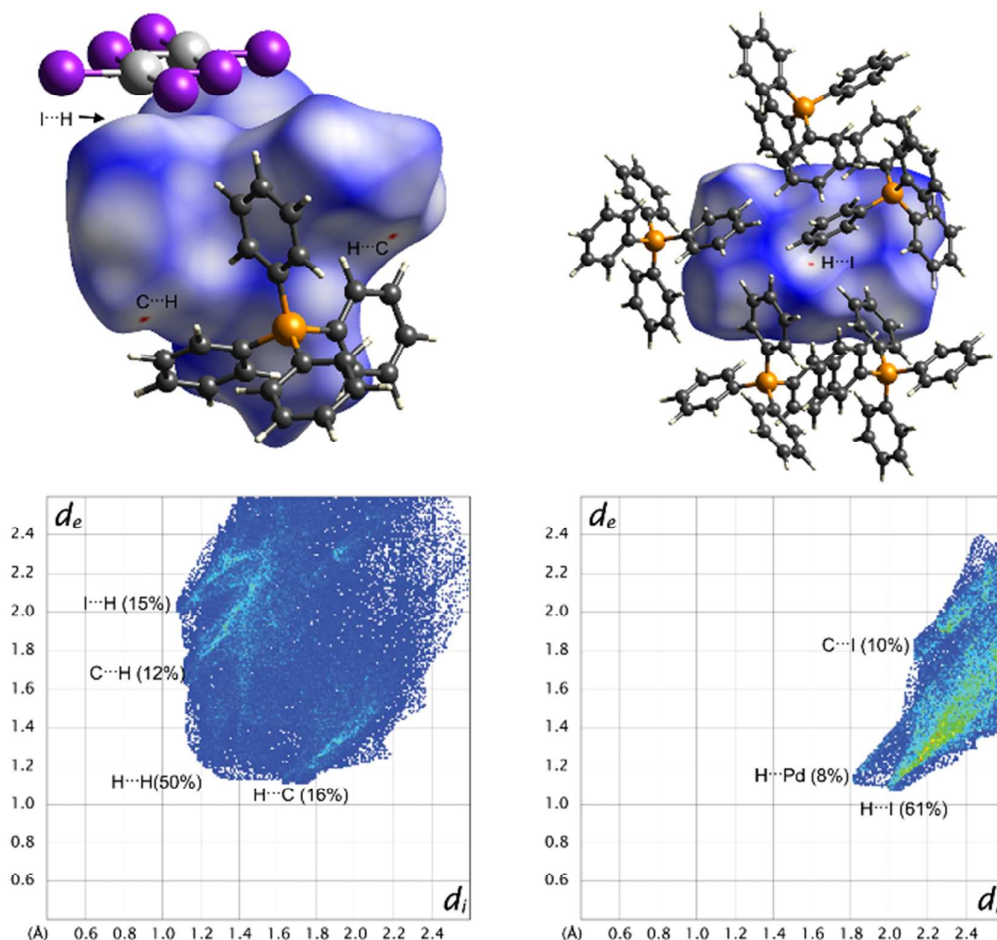
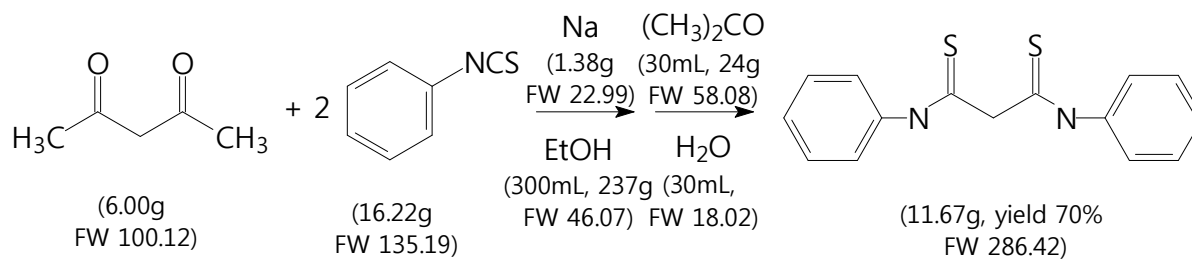


Figure S11. Hirshfeld surface (HS) and fingerprint plots of $(\text{Ph}_4\text{P})_2[\text{Pd}_2\text{I}_6]$ (**4**). Left, cation Ph_4P^+ ; right, anion $[\text{Pd}_2\text{I}_6]^{2-}$.§

§ Red spots on HS represent contacts between interacting fragments, d_e and d_i represent the distance from the HS to the nearest nucleus outside or inside, respectively, the surface. Color codes varying from blue to red highlight the frequency with which a (d_e , d_i) is observed.

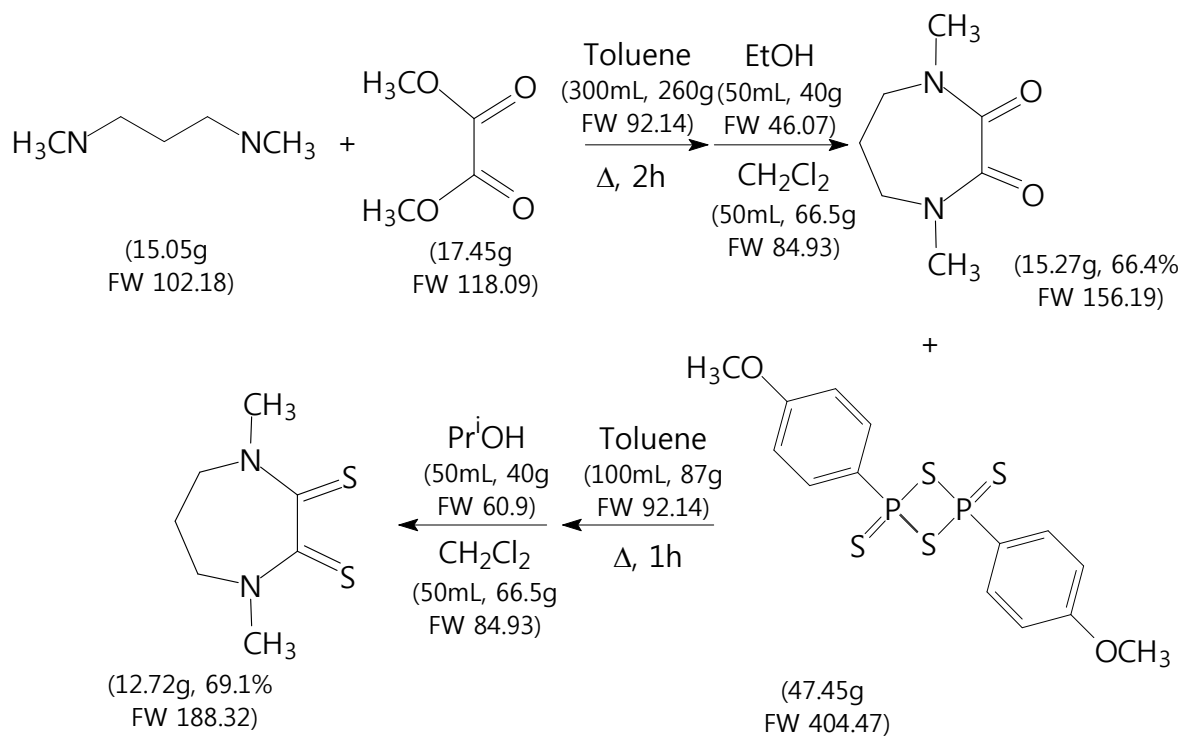
Sustainability metrics for (PhHN)₂DTM and Me₂dazdt ligands^[S1]



Scheme S1. Synthesis of (PhHN)₂DTM

Table S3. Sustainability metrics for the synthesis of (PhHN)₂DTM ligand.

Parameter	Eqn.	Numerator	Denominator	Result
Atom Economy (%)	$\frac{\text{FW desired product}}{\text{combined FW starting materials}} \times 100$	286.42	$100.12 + (2 \times 135.19) = 370.5$	77%
E-Factor	$\frac{\text{Kg (waste)}}{\text{Kg (product)}} = \frac{\text{Amount (reactants - desired product)}}{\text{Amount desired product}}$	$(6.00 + 16.22 + 1.38 + 237 + 24 + 30) - 11.67 = 302.93$	11.67	26
Effective Mass Yield (%)	$\frac{\text{mass of desired products}}{\text{mass of non-benign reagents}} \times 100$	11.67	16.22	72%



Scheme S2. Synthesis of Me₂dazdt.

Table S4. Sustainability metrics for the synthesis of Me₂dazdt ligand.

Parameter	Eqn.	Numerator	Denominator	Result
Atom Economy (%)	$\frac{\text{FW desired product}}{\text{combined FW starting materials}} \times 100$	188.32	$102.18 + 118.09 + (1.2 \times 404.47) = 705.63$	27%
E-Factor	$\frac{\text{Kg (waste)}}{\text{Kg (product)}} = \frac{\text{Amount (reactants - desired product)}}{\text{Amount desired product}}$	$(15.05 + 17.45 + 260 + 40 + 66.5 + 47.45 + 87 + 40 + 66.5) - 12.72 = 616$	12.72	48
Effective Mass Yield (%)	$\frac{\text{mass of desired products}}{\text{mass of non-benign reagents}} \times 100$	12.72	$260 + (66.5 \times 2) + 87 = 477$	3%

All three selected parameters agree with a “greener” character of (PhHN)₂DTM ligand.

[S1] D. J. C. Constable, A. D. Curzons, V. L. Cunningham, Green Chemistry, 2002, 4, 521–527

Synthesis and characterization of ligands and salts

(PhHN)₂DTM and Mo₂DTM ligands, and Mo₂DTLI₃ salt were prepared according to reported procedures (refs 33 and 20 in the main text). (PhHN)₂DTLI₃ salt was prepared as described below.

(PhHN)₂DTM. Metal sodium (1.38 g, 60 mmol) was dissolved in about 300 mL of EtOH, under stirring at room temperature for 1h. Acetylacetone (6 g, 60 mmol) and phenyl isothiocyanate (16.22 g, 120 mmol) were added to the clear solution under stirring. The color of the solution turned from yellow to orange in about 20 hours. A fast precipitation of the deep yellow crude product was achieved by adding distilled water to the solution. The crude product was then re-crystallized from acetone and distilled water obtaining yellow needle-shaped crystals. Reaction yield: 66%.

CHN % found (*calculated for C₁₅H₁₄N₂S₂, FW=286.42*): C 64.13 (62.90); H 5.27 (4.93); N 9.53 (9.78);

IR (KBr pellet, cm⁻¹): 3450bw; 3180s; 3120vw; 3000w; 1702w; 1618w; 1516s; 1496s; 1444w; 1395vs; 1213w; 1115s; 1071w; 1026w; 969vw; 907vw; 848vw; 760m; 715s; 680s; 613; 501m.

UV-visible [λ , nm (ϵ , dm³mol⁻¹cm⁻¹)]: 382.97 (2700); 300.93 (19700).

Mo₂DTM. Morpholine (4 g, 46 mmol) and malonyl chloride (1.57 g, 11 mmol) were dissolved separately in a little volume of CHCl₃. The malonyl chloride solution was added, drop by drop, to the morpholine solution under stirring at room temperature. A fast precipitation of a whitish precipitate of morpholine hydrochloride, occurred and removed from the solution by filtration. A H₂O/CHCl₃ liquid/liquid extraction was performed in order to eliminate residual unreacted reagents. Dimorpholymalonamide was recovered from the solution by evaporation of the solvent and washing with Et₂O. The white solid was then solforated in refluxing toluene by using Lawesson's reagent in a 1:1.2 molar ratio, for 4h. Dimorpholyldithiomalonamide was recovered in almost quantitative yield, by evaporation of toluene and re-crystallized from CH₂Cl₂/EtOH.

IR (KBr pellet, cm⁻¹): 3440w, 2960vw, 2910w, 2850w, 1480m, 1430m, 1383s, 1323w, 1303w, 1273m, 1237vw, 1227m, 1207vw, 1183m, 1110s, 1060m, 1027m, 950m, 923m, 890m, 850vw, 820vw, 723vw, 690vw, 617m, 547w, 500w.

UV-vis [λ , nm (ϵ , dm³mol⁻¹cm⁻¹)]: 284.43(33000).

Mo₂DTLI₃. This salt was prepared as described above, starting from Mo₂DTM (0.311 g, 1.1 mmol) and I₂ (0.542 g, 2.2 mmol) in CH₂Cl₂. A quick precipitation of purple crystals of the product is observed with the reaction. Reaction yield: 50%.

CHN % found (*calculated for C₁₁H₁₇I₃O₂N₂S₂+H₂O FW=672.12*): C 19.5 (19.66); H 2.8 (2.85); N 4.0 (4.17);

IR (KBr pellet, cm⁻¹): 3090w, 2970w, 2860w, 1539vs, 1458vw, 1427m, 1368m, 1353, 1329w, 1302m, 1267s, 1224, 1108s, 1061m, 867m, 746m, 614m.

UV-vis [λ , nm (ϵ , dm³mol⁻¹cm⁻¹)]: 291.51(136500); 361.99(60200).

(PhHN)₂DTLI₃. (PhHN)₂DTM (9 g, 31 mmol) and I₂ (16 g, 63 mmol) were dissolved separately in a little volume of (CH₃)₂CO and then mixed and reacted under stirring at room temperature for about 30 minutes. Brown needle-shaped crystals of the product suitable for X-ray analysis were obtained by slow Et₂O diffusion into the reaction solution. Reaction yield: 60%.

CHN % found (*calculated for C₁₅H₁₃I₃N₂S₂+2/3CH₃COCH₃, FW=704.83*): C 30.69 (29.41); H 2.70 (2.47); N 4.29 (4.03);

IR (KBr pellet, cm⁻¹): 3240m, 3050w, 2950w, 1594s, 1524vs, 1477vs, 1411s, 1200s, 1077w, 1026w, 905w, 781s, 754s, 707m, 688m, 657w, 606w, 579w, 552m, 513w, 497w, 478w.

UV-vis [λ , nm (ϵ , dm³mol⁻¹cm⁻¹)]: 349.52 (35500) ;294.47 (46300); 244.17 (19100).

¹H-NMR (δ , ppm; DMSO-*d*₆): 11.73(s), 7.47(m), 6.67(s).