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Diamondoid architectures from halogen-bonded halides

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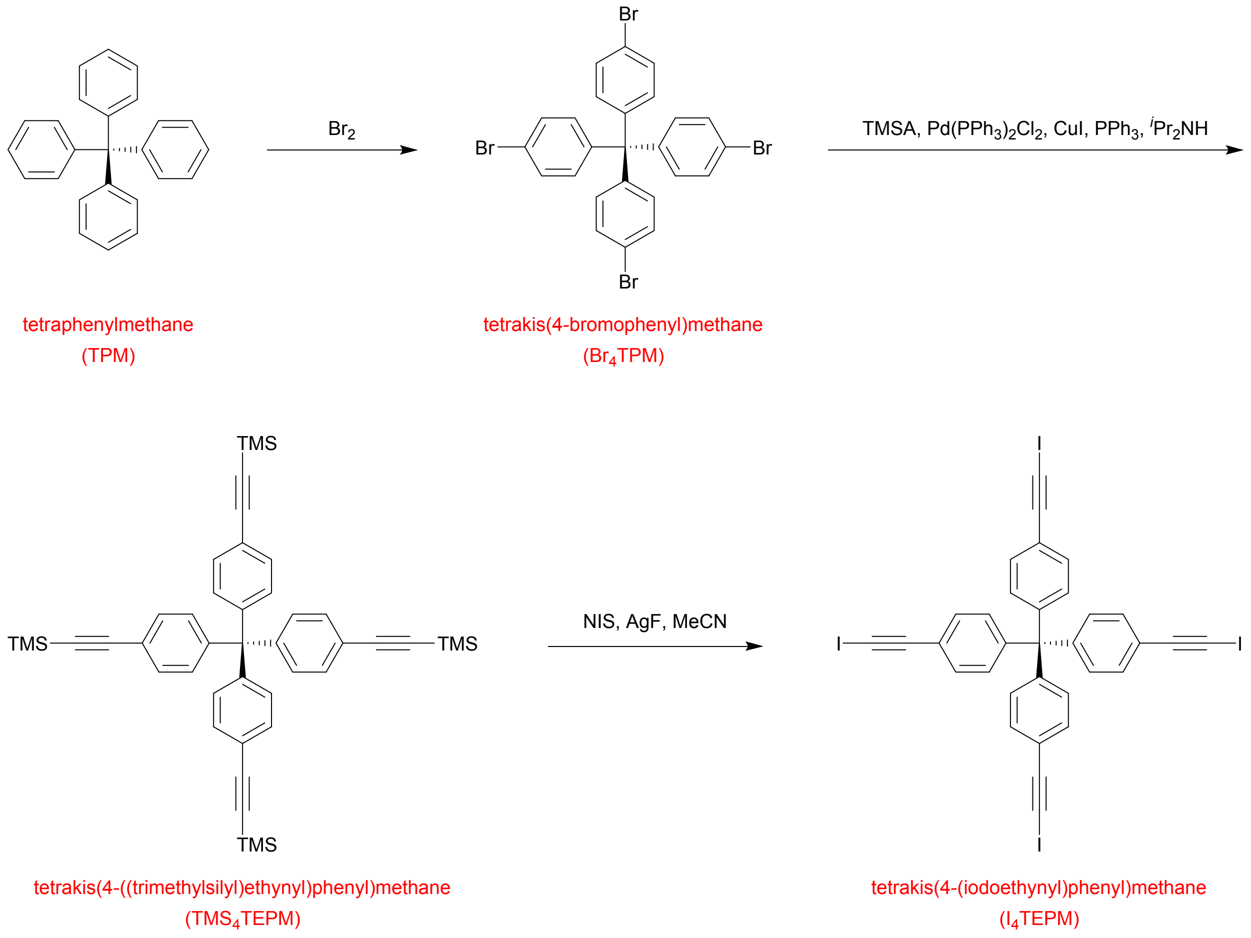
Supplementary Information

CONTENTS

Experimental

Materials and methods

All the reagents, solvents, halide salts and tetraphenylmethane were purchased from commercial sources, and were used as received without further purification. Nuclear magnetic resonance spectra were recorded on a Varian Unity Plus (400 MHz) NMR spectrometer. A Nicolet 380 FT-IR system was used for the infrared spectroscopic analysis. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on TA Instruments TA Q20 and TA Q50, respectively.



Scheme S1: Synthetic route to I_4TEPM.

Synthesis of tetrakis(4-bromophenyl)methane, Br_4TPM

The bromination of tetraphenylmethane was performed neat using an excess of molecular bromine. To a 100-mL round-bottom flask containing tetraphenylmethane (2.00 g, 6.24 mmol, 1 equiv.), bromine liquid (6.4 mL, 124.8 mmol, 20 equiv.) was added carefully at 0 °C. After attaching a water-cooled reflux condenser, the resultant dark reddish slurry was stirred vigorously at room temperature for one hour, and then cooled to −78 °C by using a dry ice/acetone bath. Ethanol (25 mL) was added slowly and the reaction mixture was allowed to warm to room temperature overnight. Then, to destroy excess/unreacted bromine, it was treated with 40% aqueous solution of sodium bisulfite (approximately 75 mL) and stirred for additional 30 minutes until the orange color disappeared. The tan colored solid was collected by filtration, washed well with distilled water (100 mL) and oven-dried at 60 °C for five hours. This solid was further purified by re-crystallization from chloroform/ethanol (2:1), affording tetrakis(4-bromophenyl)methane, **Br_4TPM** as an off-white crystalline material. Yield: 3.65 g (5.74 mmol, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39 (d, 8H); 7.01 (d, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.64, 132.57, 131.30, 121.02, 63.84.

Synthesis of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane, TMS_4TEPM

This step involved a Sonogashira cross-coupling reaction of tetrakis(4-bromophenyl)methane with trimethylsilylacetylene. Tetrakis(4-bromophenyl)methane (3.50 g, 5.50 mmol, 1 equiv.) and triphenylphosphine (462 mg, 1.76 mmol, 32 mol%) were placed in a 250-mL round-bottomed flask. Diisopropyl amine (100 mL) was added and the resulting solution was purged with dinitrogen gas for 30 minutes. Then, bis(triphenylphosphine)palladium(II) dichloride (618 mg, 0.88 mmol, 16 mol%), copper(I) iodide (168 mg, 0.88 mmol, 16 mol%) and trimethylsilylacetylene (6.2 mL, 44.0 mmol, 8 equiv.) were added. The reaction flask was fitted to a water-jacketed condenser, cooled to −78 °C, subjected to a brief vacuum/backfill cycle and refluxed for 24 hours under nitrogen atmosphere. After removing volatile materials *in vacuo*, the residue was re-dissolved in chloroform (100 mL) and filtered through a pad of Celite, using an extra 50 mL portion of chloroform to wash the filter pad. The combined filtrate was then washed with distilled water (2 × 25 mL) and brine (25 mL), dried over anhydrous magnesium sulfate, and evaporated to dryness under vacuum. Crude product was flash-column-chromatographed on silica gel using pure hexanes followed by hexanes/ethyl acetate (4:1) as eluents to obtain the title compound,

TMS$_4$TEPM as a pale yellowish solid. Yield: 3.30 g (4.68 mmol, 85%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.33 (d, 8H), 7.05 (d, 8H), 0.24 (s, 36H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 146.21, 131.59, 130.95, 121.42, 104.82, 95.00, 64.98, 0.18.

Synthesis of tetrakis(4-(iodoethynyl)phenyl)methane, I$_4$TEPM

The one-pot/*in situ* desilylative iodination (*i.e.* direct trimethylsilyl-to-iodo conversion) method was employed. Acetonitrile (150 mL) was transferred into a 250-mL round-bottom flask that contained tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane (2.50 g, 3.54 mmol, 1 equiv.). The flask was wrapped in aluminium foil, and then silver(I) fluoride (2.70 g, 21.3 mmol, 6 equiv.) and *N*-iodosuccinimide (4.78 g, 21.3 mmol, 6 equiv.) were added. It was evacuated (while stirring), refilled with nitrogen and stirred at room temperature for 24 hours. Distilled water (200 mL) was added and the resulting mixture was extracted with diethyl ether (4 × 50 mL). The combined organic layers were washed with saturated sodium bisulfite (40 mL), distilled water (40 mL) and brine (40 mL), and dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure resulted in an orange colored residue. Additional cleanup by column chromatography (silica gel, hexanes/ethyl acetate = 9:1) gave the desired compound, **I$_4$TEPM**, as a yellow solid. Yield: 1.83 g (1.98 mmol, 56%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.32 (d, 8H), 7.06 (d, 8H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 146.34, 132.04, 130.87, 121.81, 93.87, 65.02, 7.03. ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.37 (d, 8H), 7.04 (d, 8H). ^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 145.68, 131.66, 130.36, 121.08, 92.11, 64.26, 18.41.

Synthesis of I$_4$TEPM·Ph$_4$P$^+$Cl$^-$ complex

In a 2-dram glass vial with a screw cap, **I$_4$TEPM** (10 mg, 0.011 mmol, 1 equiv.) was dissolved in 0.5 mL of chloroform. Then, Ph$_4$P$^+$Cl$^-$ (4.1 mg, 0.011 mmol, 1 equiv.) in 0.5 mL of methanol was carefully added on top, with minimal agitation to prevent the product from crashing out at the interface. The vial was sealed and left undisturbed at ambient conditions to allow the two solutions to diffuse together slowly. Yellowish orange crystals suitable for single-crystal X-ray diffraction were observed after two days. Decomposition temperature: 235–250 °C.

Synthesis of $\mathbf{I_4TEPM \cdot Ph_4P^+Br^-}$ complex

Our initial attempt of preparing single-crystals of title compound in the same way as $\mathbf{I_4TEPM}\cdot Ph_4P^+Cl^-$ was failed due to instant product precipitation. Therefore, both starting solutions were subjected to two-fold dilution, and an intermediate buffer layer of methanol was placed between them to further decelerate their mixing. $\mathbf{I_4TEPM}$ (10 mg, 0.011 mmol, 1 equiv.) was dissolved in 1 mL of chloroform. After careful layering of 10 drops of neat methanol, $Ph_4P^+Br^-$ (4.6 mg, 0.011 mmol, 1 equiv.) in 1 mL of methanol was slowly added on top without disturbing the interface. The vial was then sealed and allowed to stand at room temperature. Yellowish orange crystals suitable for single-crystal X-ray diffraction were appeared in 24 hours. Decomposition temperature: 230–250 °C.

Synthesis of $\mathbf{I_4TEPM \cdot Ph_4P^+I^-}$ complex

Yellowish orange crystals suitable for single-crystal X-ray diffraction were obtained within 10 hours by following the same solution layering (reactant diffusion) technique mentioned above for $\mathbf{I_4TEPM}\cdot Ph_4P^+Br^-$, but using an equimolar amount of $Ph_4P^+I^-$ (5.1 mg, 0.011 mmol, 1 equiv.) as the halide salt. Decomposition temperature: 220–230 °C.

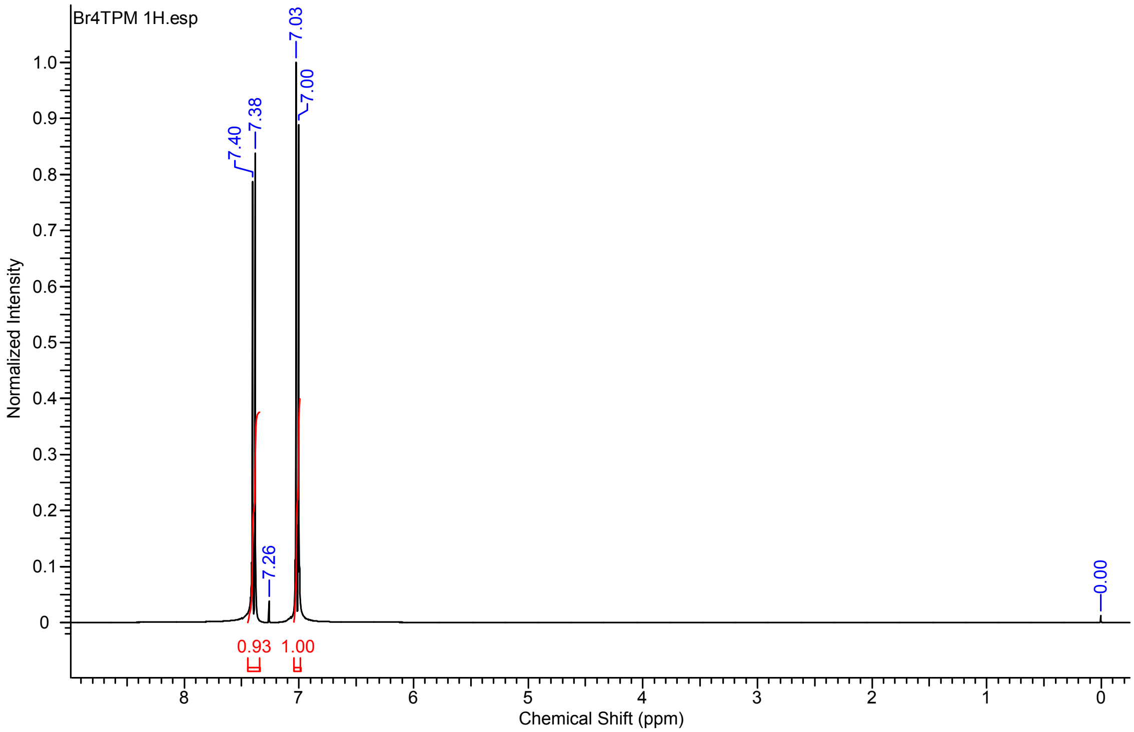


Figure S1: ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of tetrakis(4-bromophenyl)methane.

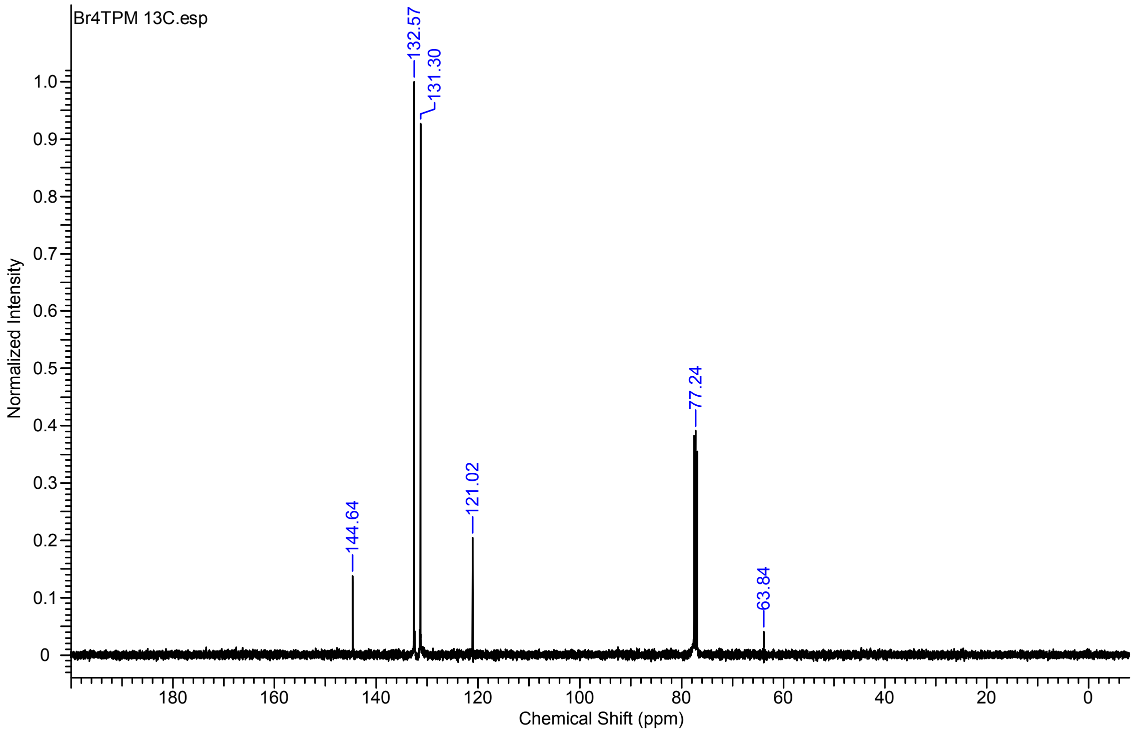


Figure S2: ^{13}C-NMR (100 MHz, CDCl$_3$) spectrum of tetrakis(4-bromophenyl)methane.

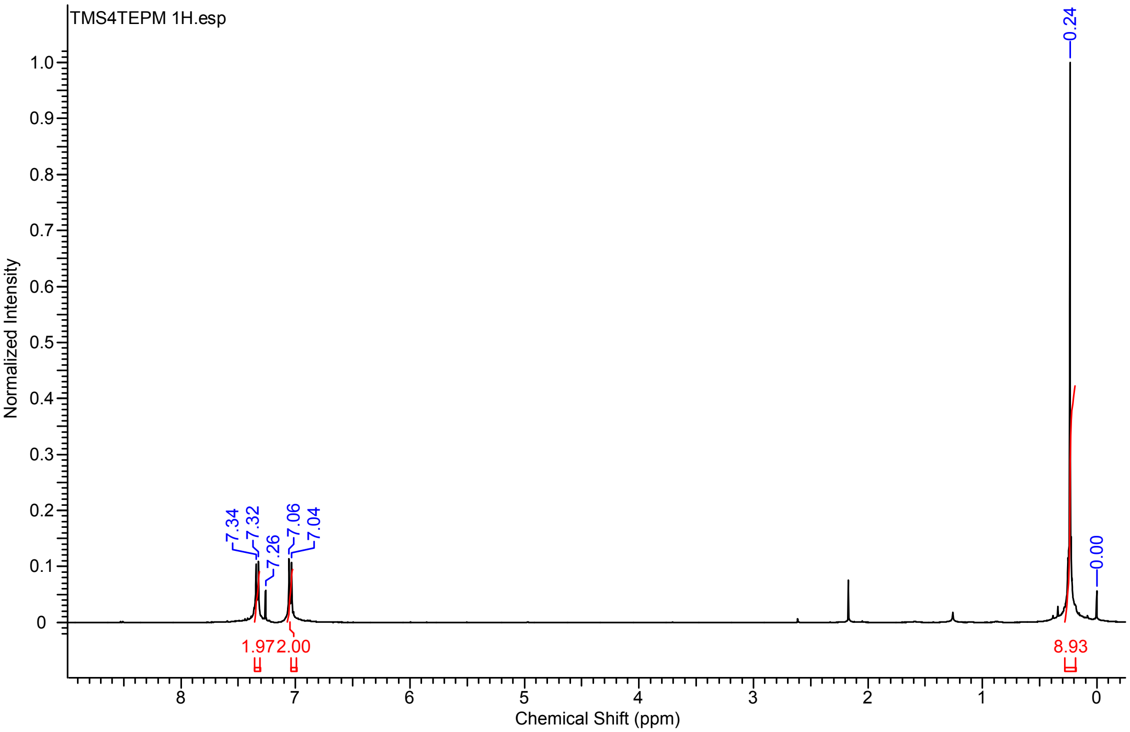


Figure S3: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane.

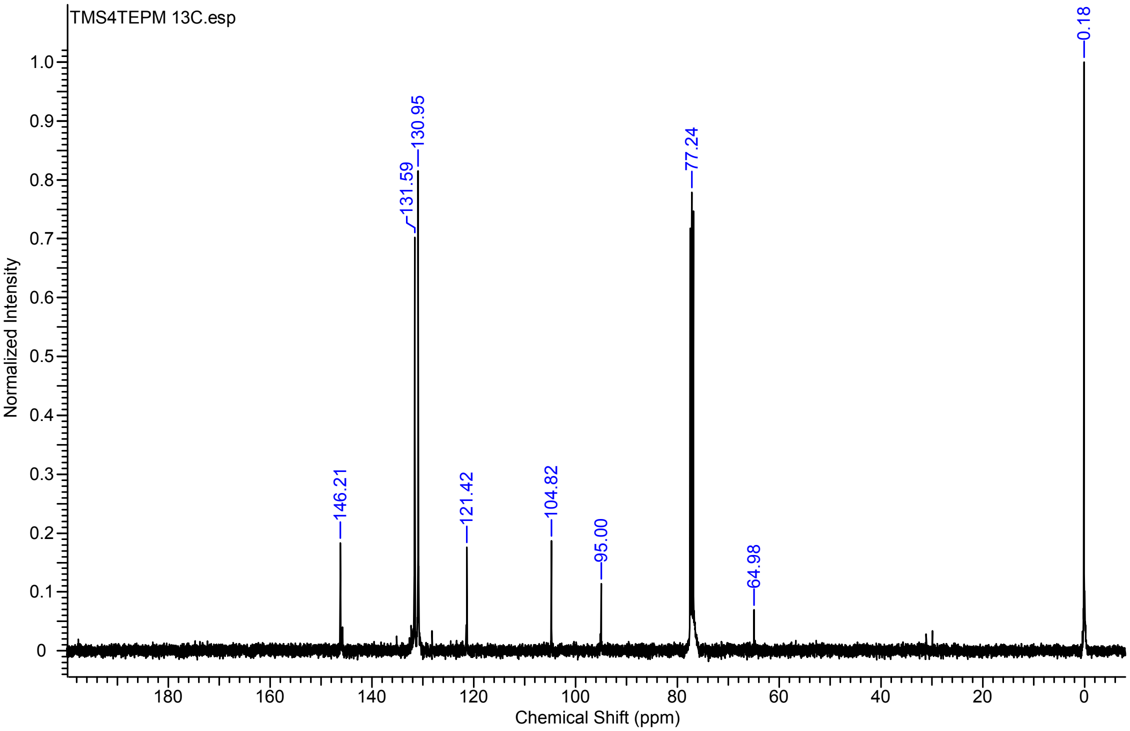


Figure S4: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane.

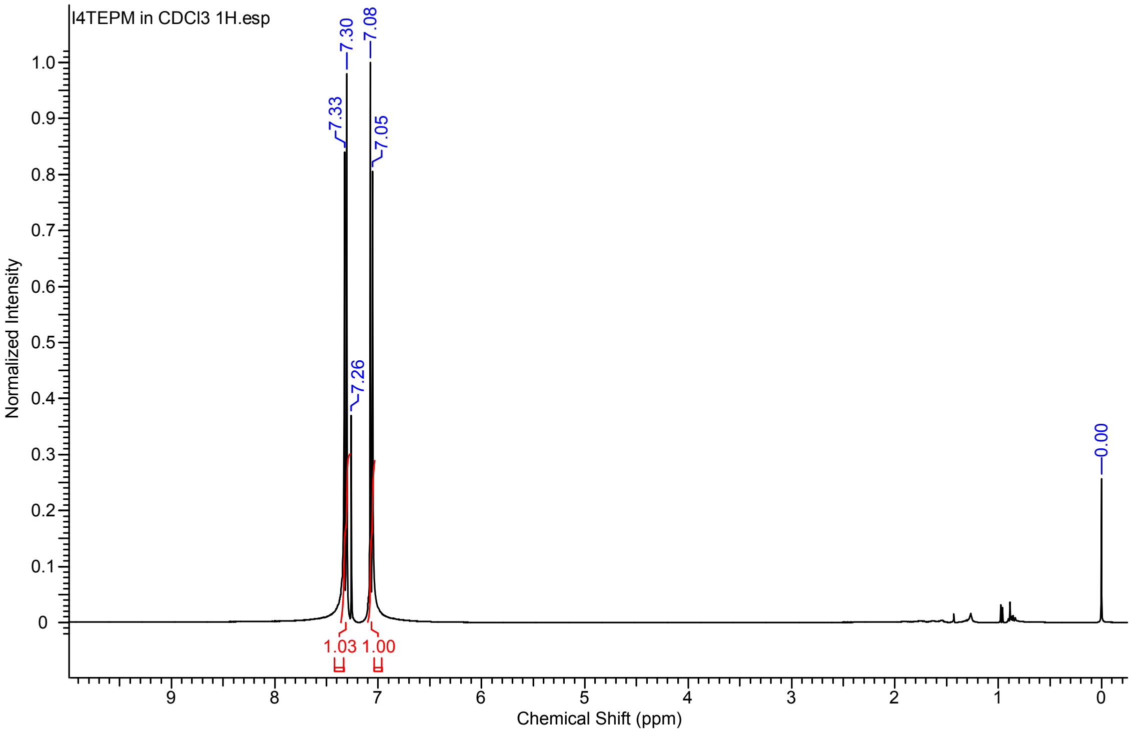


Figure S5: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of tetrakis(4-(iodoethynyl)phenyl)methane.

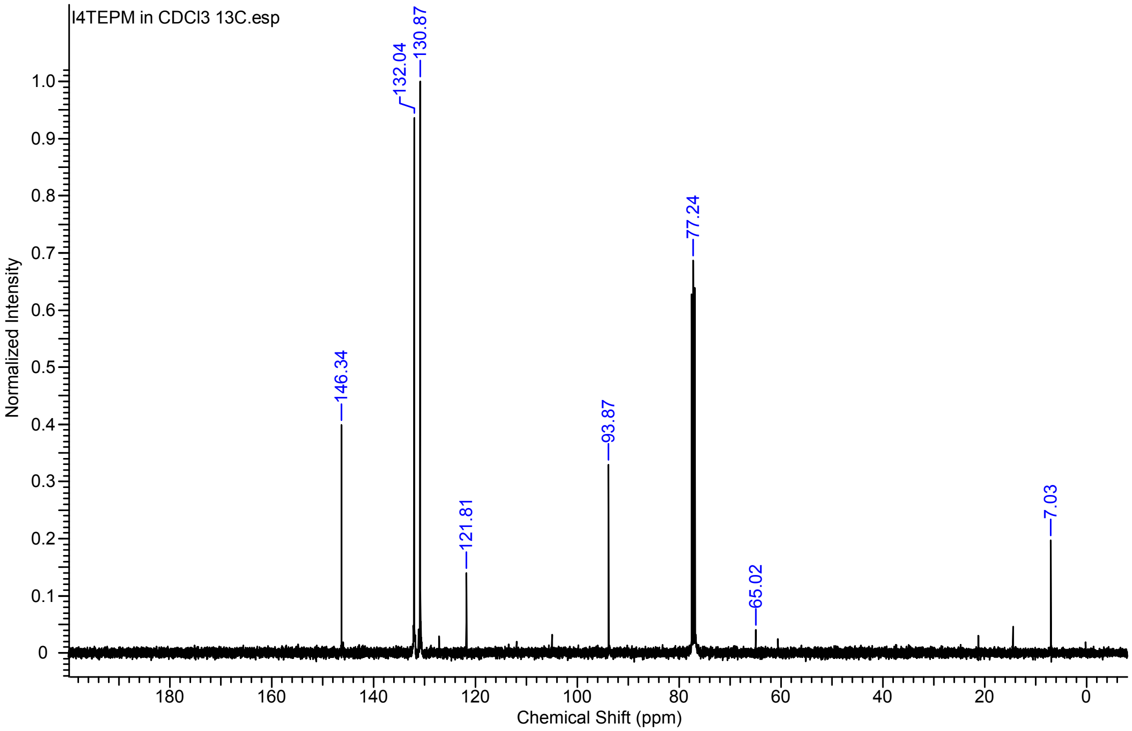


Figure S6: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of tetrakis(4-(iodoethynyl)phenyl)methane.

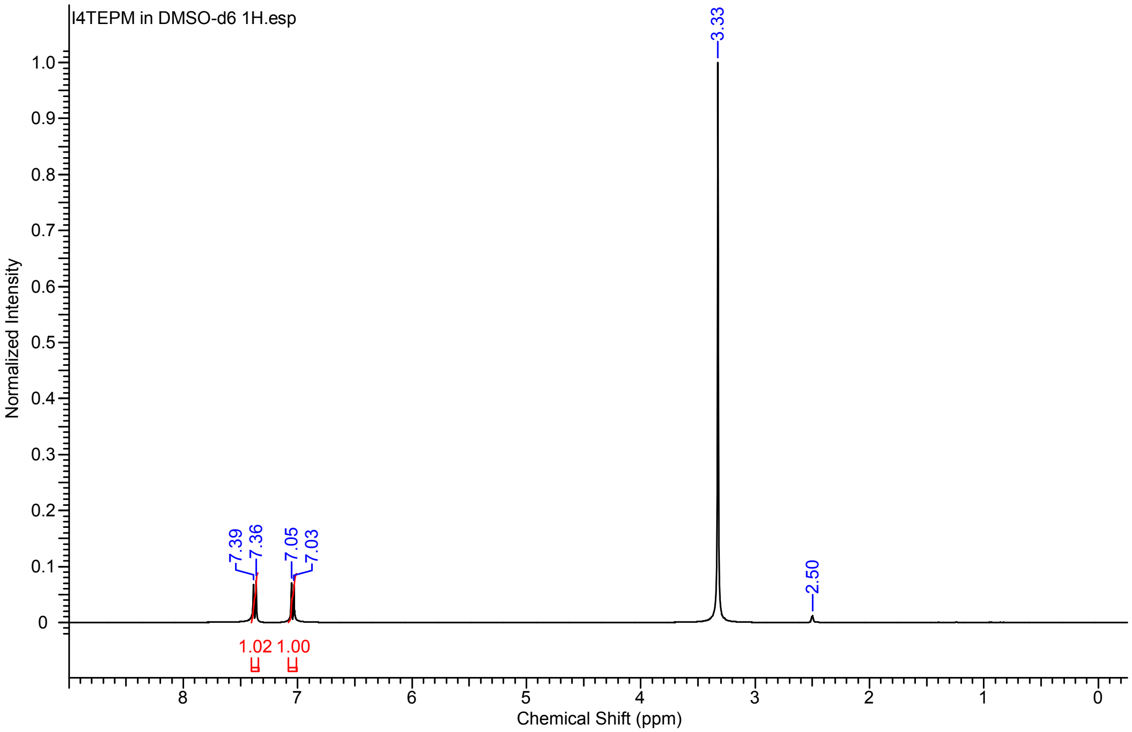


Figure S7: ^{1}H-NMR (400 MHz, DMSO-d6) spectrum of tetrakis(4-(iodoethynyl)phenyl)methane.

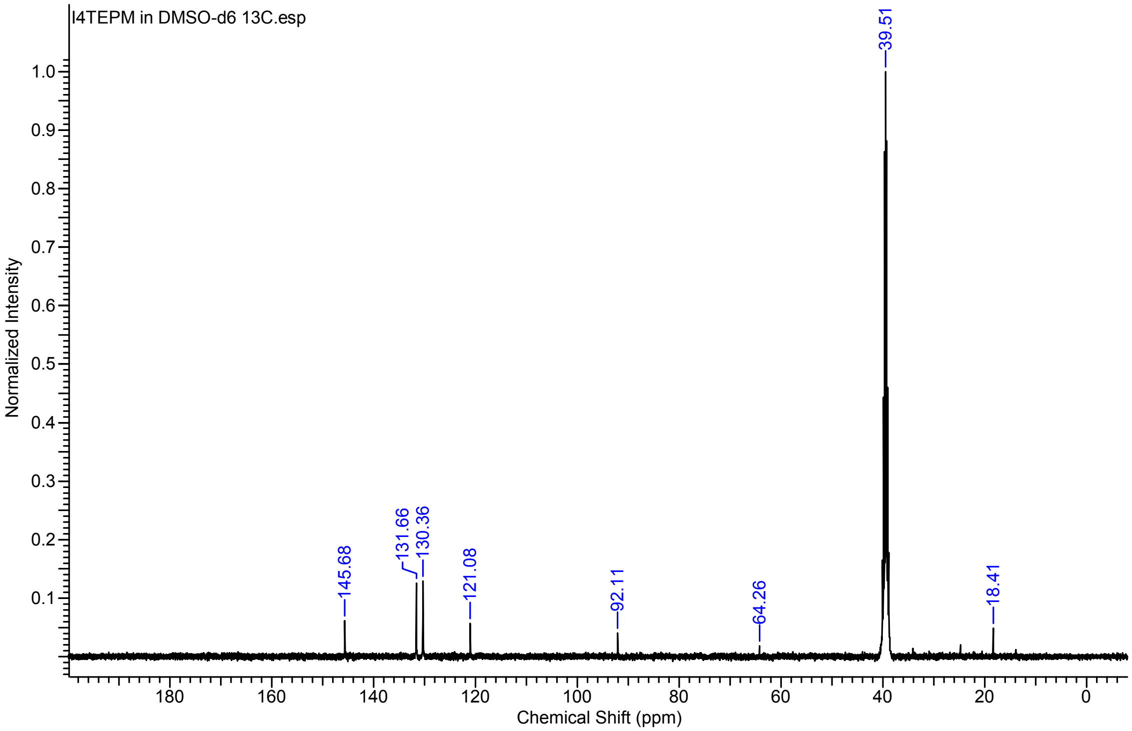


Figure S8: ^{13}C-NMR (100 MHz, DMSO-d6) spectrum of tetrakis(4-(iodoethynyl)phenyl)methane.

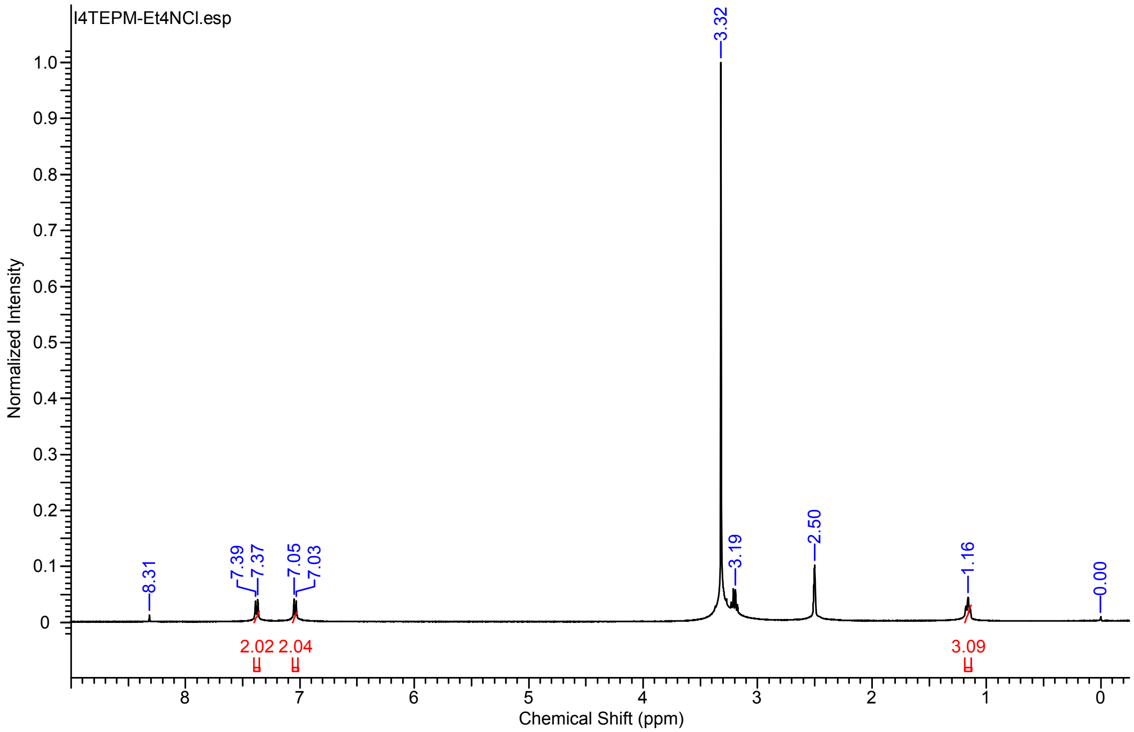


Figure S9: ^{1}H-NMR (400 MHz, DMSO-d6) spectrum of **I_4TEPM**·$Et_4N^+Cl^-$ crystals.

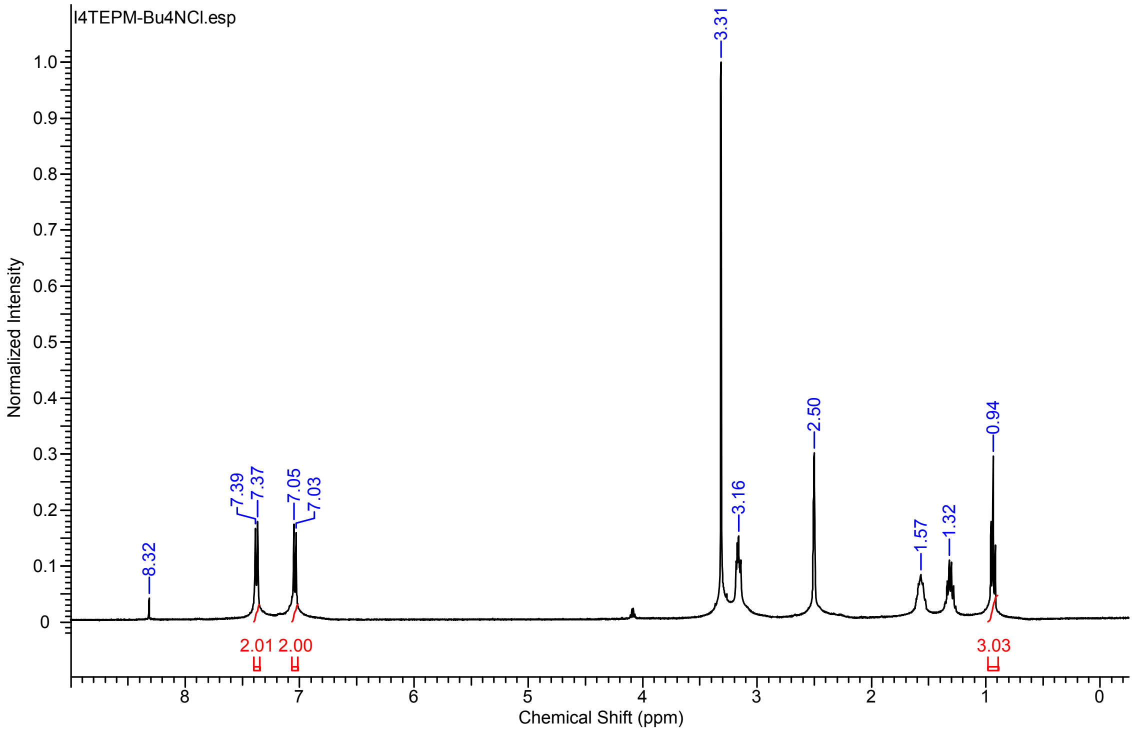


Figure S10: ^{1}H-NMR (400 MHz, DMSO-d6) spectrum of **I_4TEPM**·$Bu_4N^+Cl^-$ crystals.

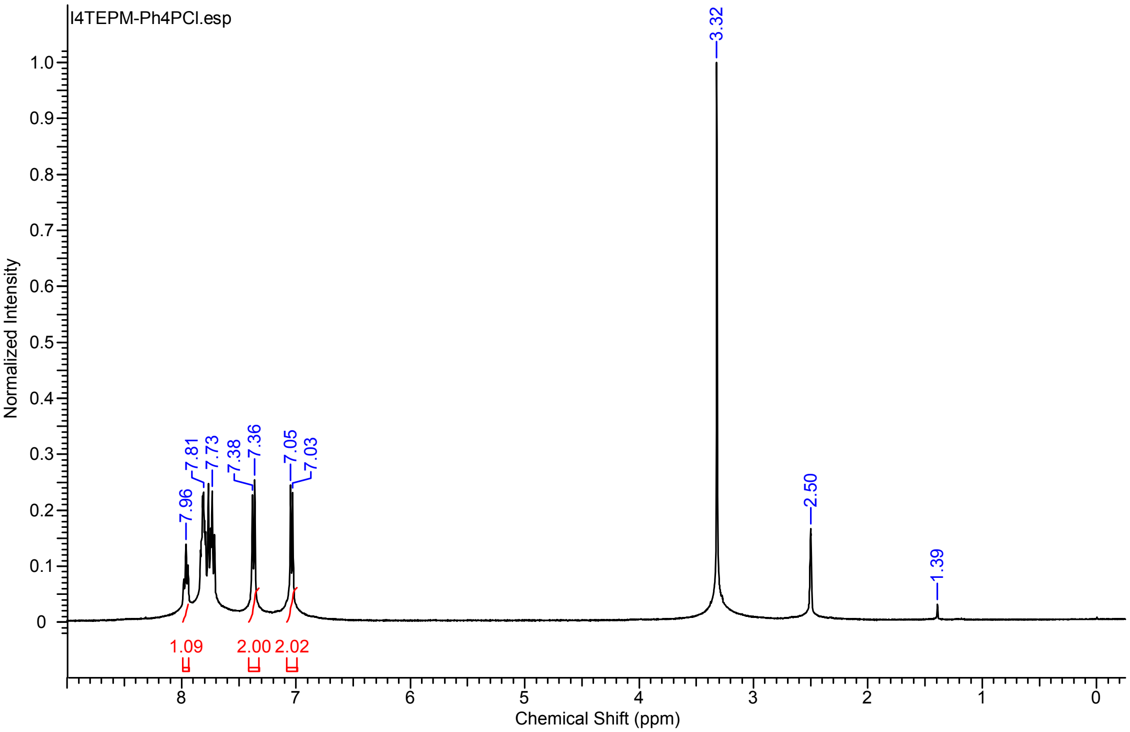


Figure S11: ^{1}H-NMR (400 MHz, DMSO-d6) spectrum of $\mathbf{I_4TEPM}\cdot Ph_4P^+Cl^-$ crystals.

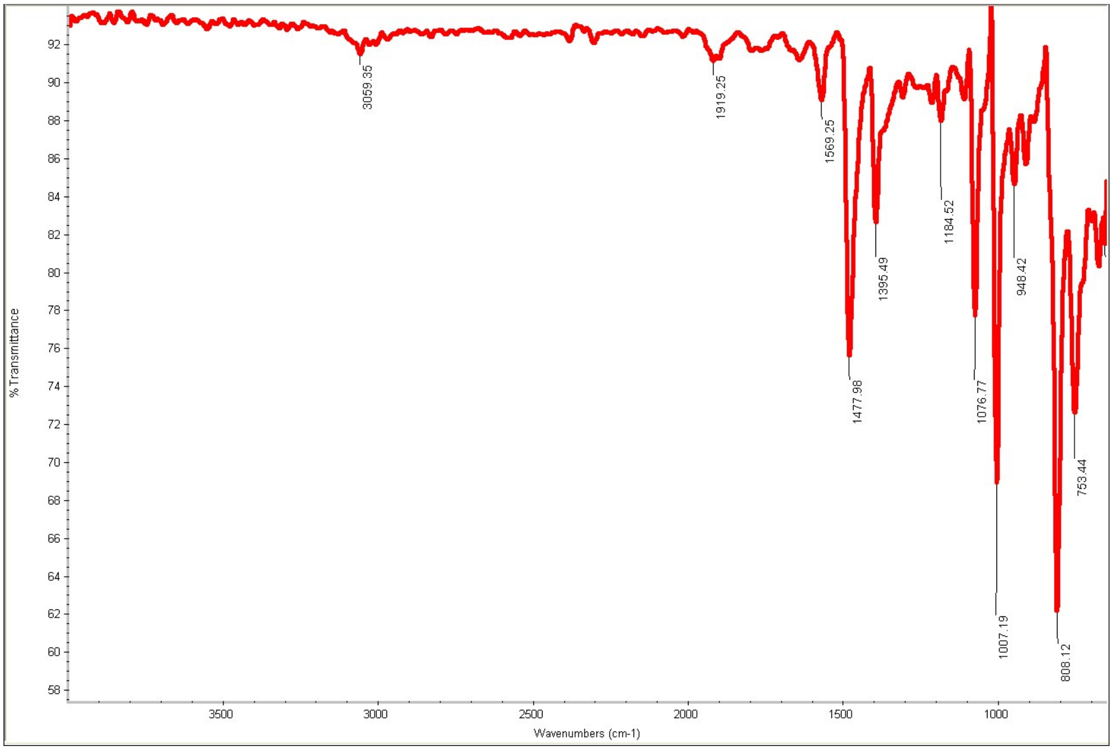


Figure S12: FT-IR spectrum of tetrakis(4-bromophenyl)methane.

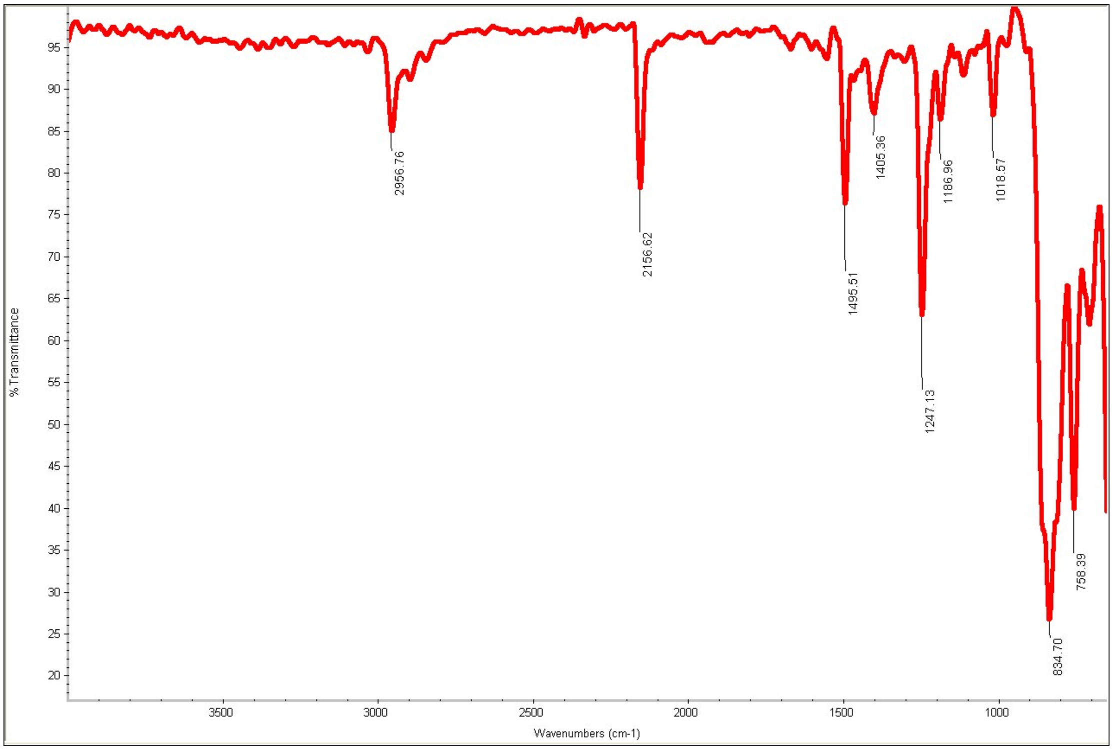


Figure S13: FT-IR spectrum of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane.

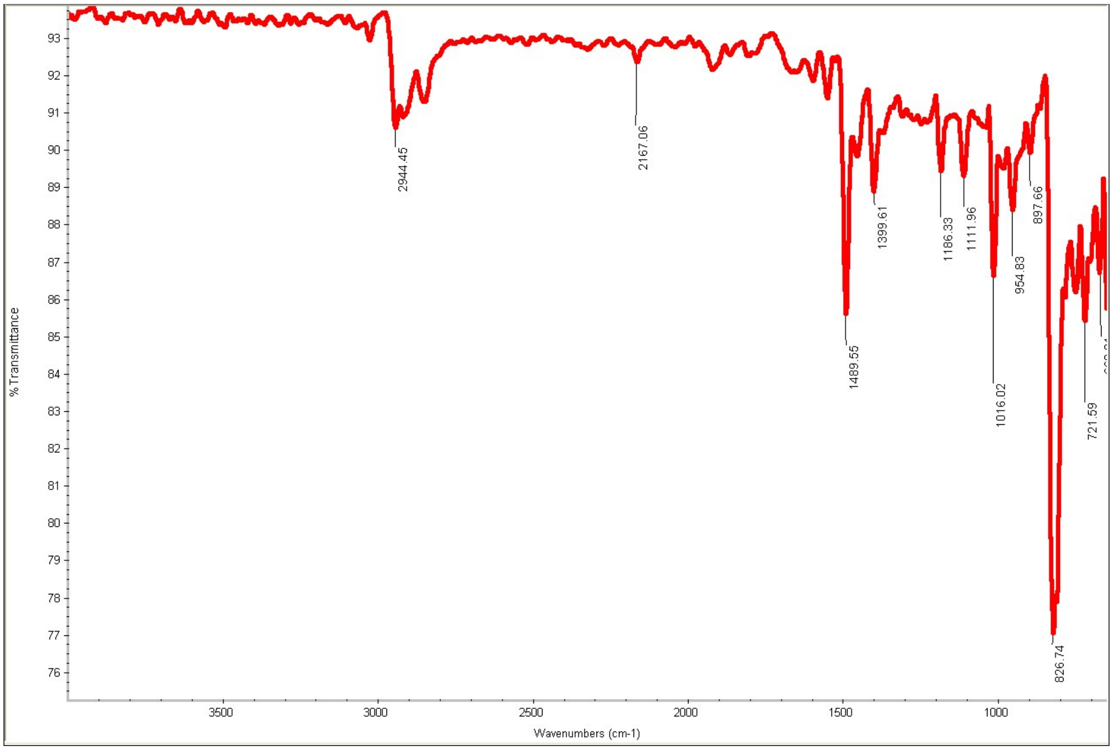


Figure S14: FT-IR spectrum of tetrakis(4-(iodoethynyl)phenyl)methane.

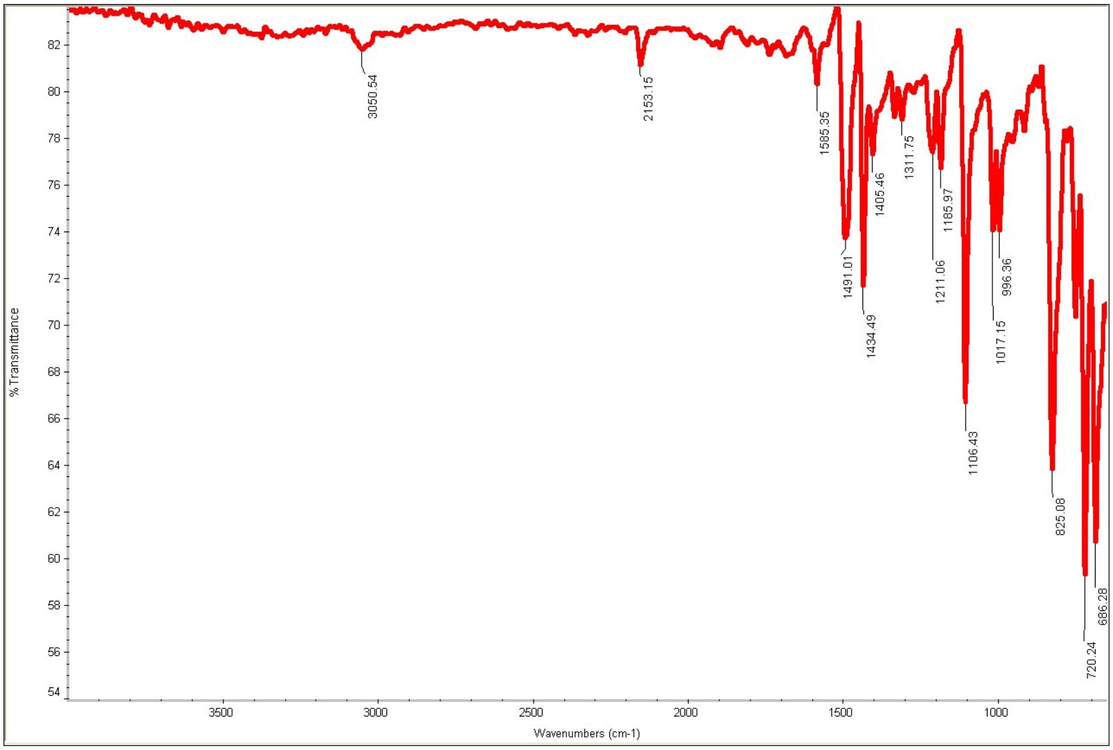


Figure S15: FT-IR spectrum of **I_4TEPM**·$Ph_4P^+Cl^-$ crystals.

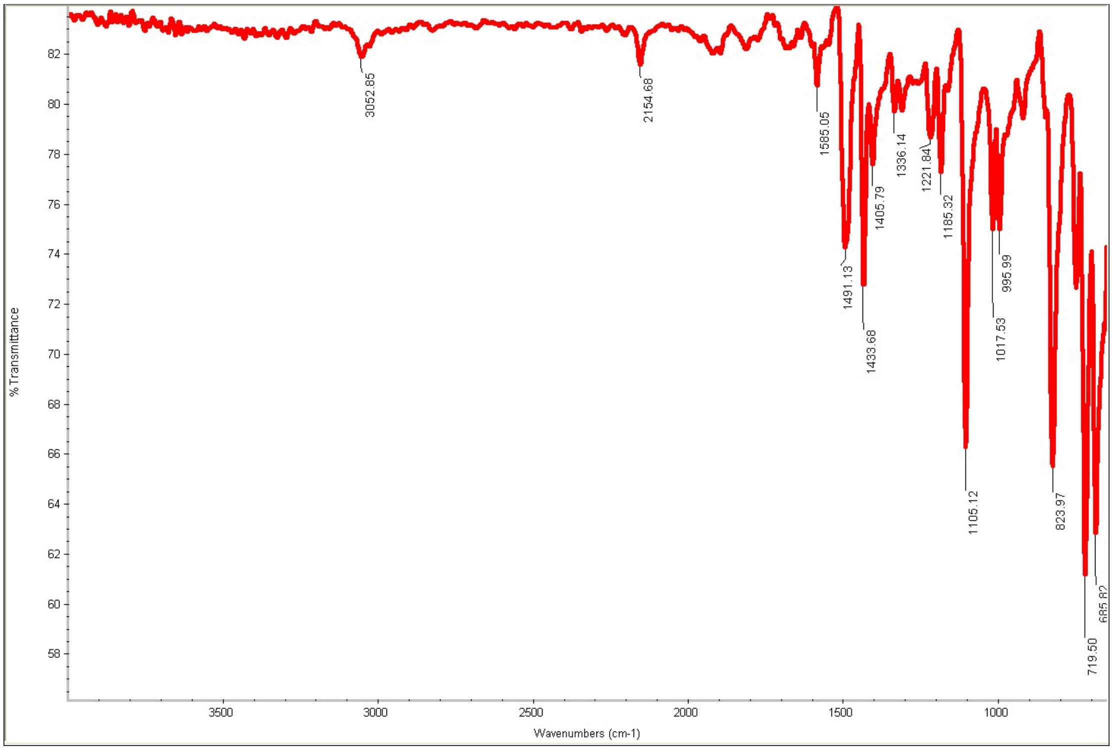


Figure S16: FT-IR spectrum of **I_4TEPM**·$Ph_4P^+Br^-$ crystals.

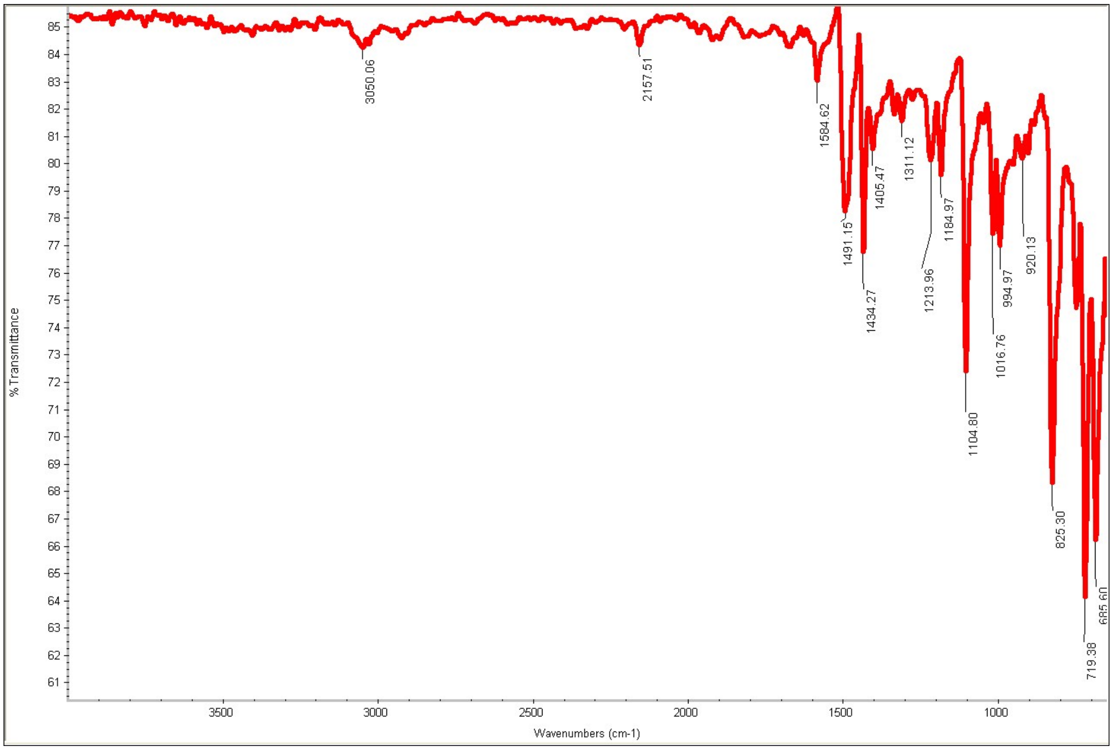


Figure S17: FT-IR spectrum of **I_4TEPM**·$Ph_4P^+I^-$ crystals.

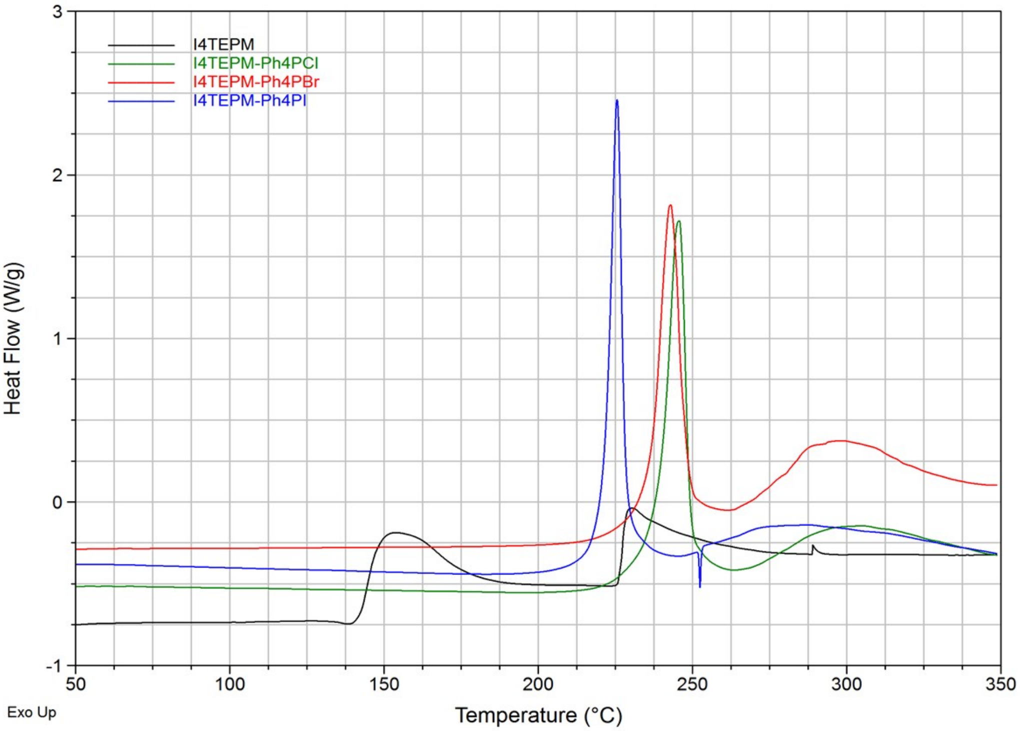


Figure S18: DSC traces (Tzero aluminum pan, 1–2 mg sample size, 5 °C·min⁻¹ heating rate, nitrogen atmosphere).

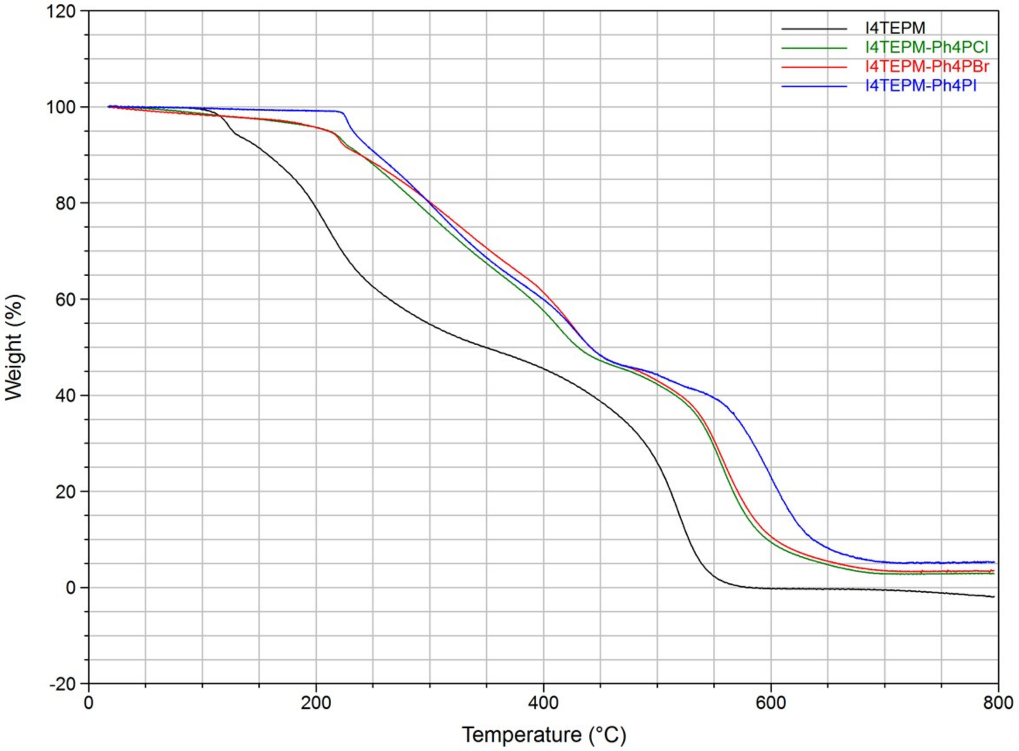


Figure S19: TGA traces (platinum pan, 5–10 mg sample size, 10 °C·min⁻¹ heating rate, nitrogen atmosphere).

Electrostatic potential calculations

In order to calculate the molecular electrostatic potentials (MEPs) of halogenated tetraphenylmethane species (**Br$_4$TPM**, **I$_4$TPM**, **Br$_4$TEPM** and **I$_4$TEPM**), first, their geometries were optimized at the hybrid functional B3LYP/6-311+G** level of theory using Spartan '14 software.[1] The visualization of MEPs was subsequently attained through mapping its values, determined with a positive point charge in the vacuum as a probe, on the molecular surface defined by an outer contour of 0.002 au electronic density. The numbers, now termed surface potentials, indicate the Coulombic interaction energies (expressed in kJ/mol) between the probe and this isodensity surface at different points.

Powder X-ray diffraction

Experiments were performed on a Philips PW 1850 diffractometer, CuKα radiation, 40 kV voltage, and 40 mA current. The patterns were collected in the region of 5°–40° (2θ) with a step size of 0.02°, and 2.0 s counting per step for **I$_4$TEPM**·Ph$_4$P$^+$I$^-$ and **I$_4$TEPM**·Ph$_4$P$^+$Br$^-$, and 6.0 s counting per step for **I$_4$TEPM**·Ph$_4$P$^+$Cl$^-$.

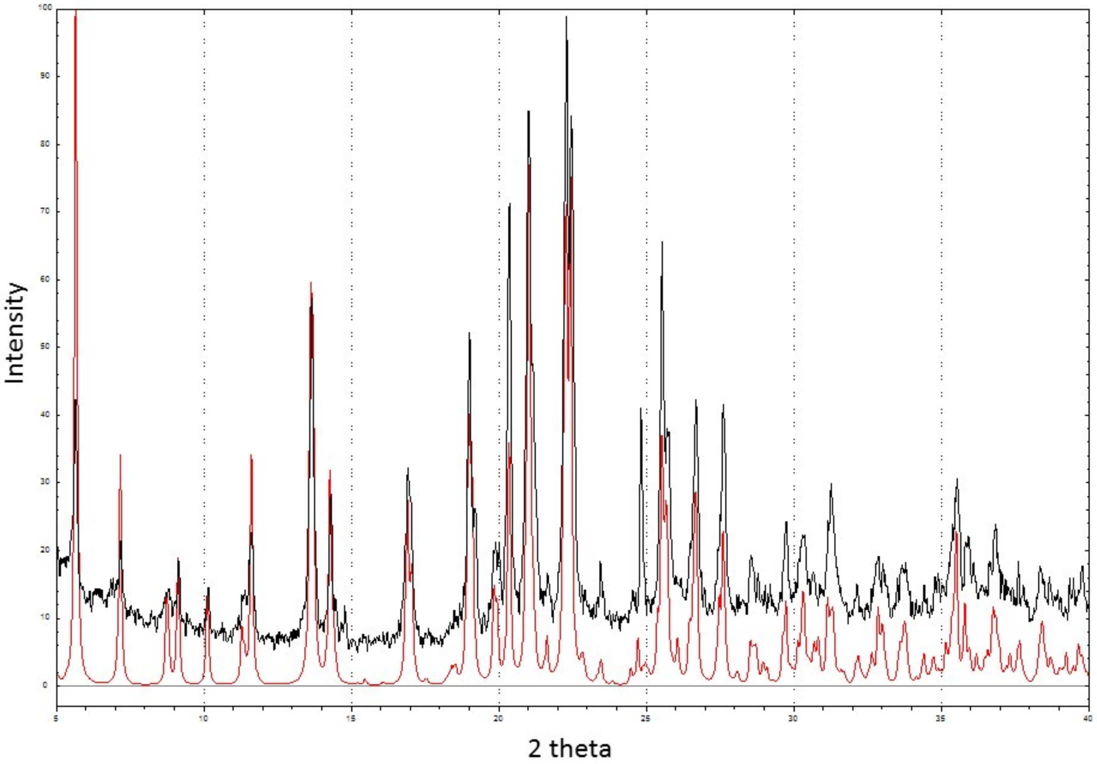


Figure S20: PXRD pattern of **I$_4$TEPM**·Ph$_4$P$^+$I$^-$ (top - experimental, bottom - simulated).

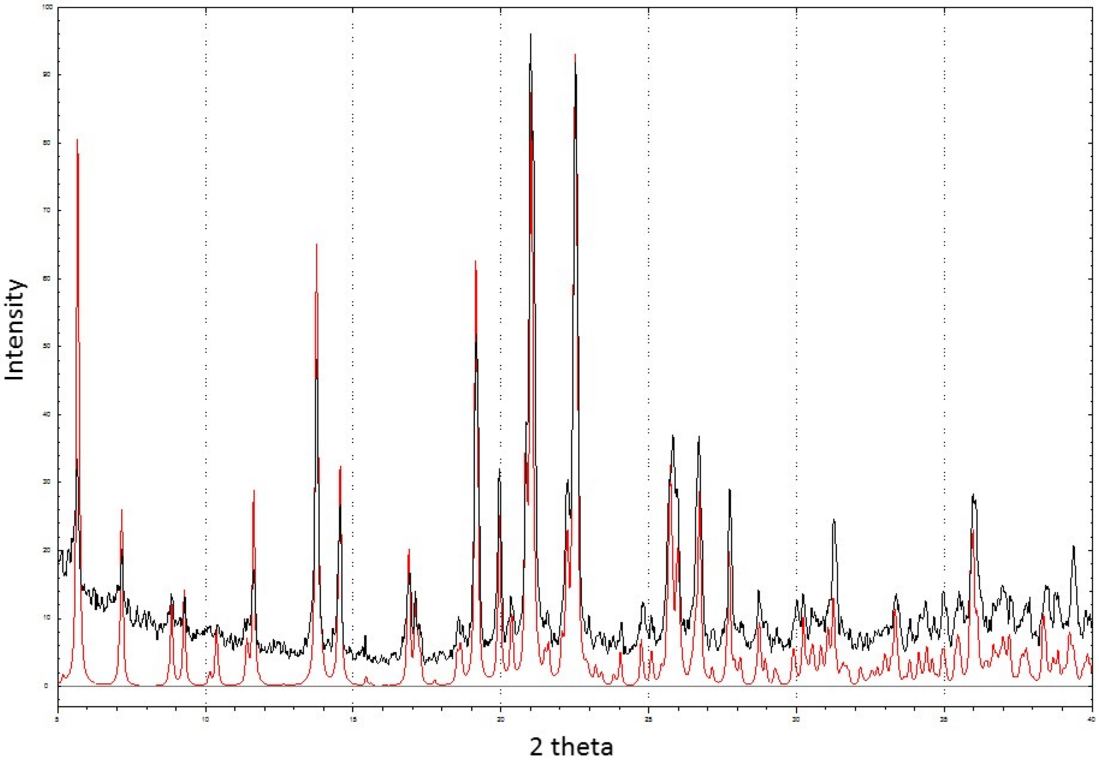


Figure S21: PXRD pattern of **I_4TEPM**·$Ph_4P^+Br^-$ (top - experimental, bottom - simulated).

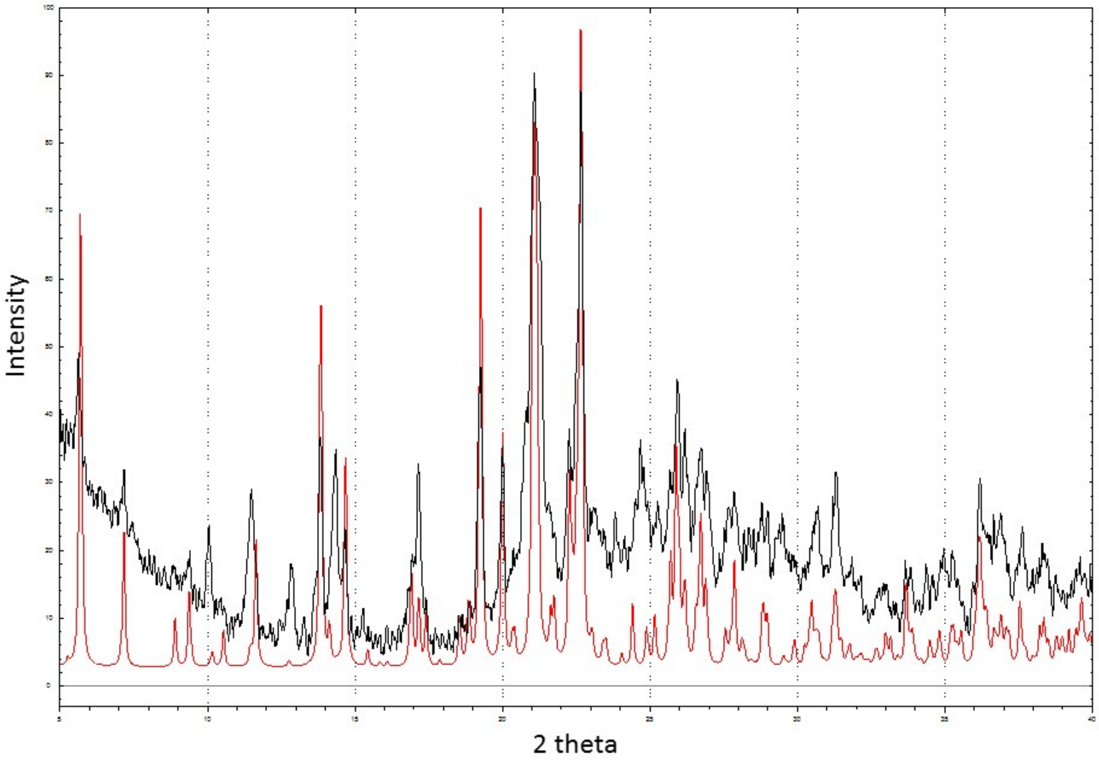


Figure S22: PXRD pattern of **I_4TEPM**·$Ph_4P^+Cl^-$ (top - experimental, bottom - simulated).

Single-crystal X-ray crystallography

Datasets for $\mathbf{I_4TEPM}\cdot Ph_4P^+Cl^-$, $\mathbf{I_4TEPM}\cdot Ph_4P^+Br^-$ and $\mathbf{I_4TEPM}\cdot Ph_4P^+I^-$ were collected on an Oxford Diffraction Xcalibur four-circle kappa geometry single-crystal diffractometer with Sapphire 3 CCD detector, using a graphite monochromated Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation, and applying the CrysAlisPro Software System[2] at 296 K. The crystal–detector distance was 45 mm. Data reduction, including Lorentz and polarization corrections as well as absorption correction, was done by CrysAlisPro program. The structure was solved by Direct methods implemented in the SHELXS-2014/7 program.[3] The coordinates and the anisotropic displacement parameters for all non-hydrogen atoms were refined by full-matrix least-squares methods based on F^2 using the SHELXL-2014/7 program. The hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their carbon atom at distance 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Table S1 gathers structural and refinement parameters for $\mathbf{I_4TEPM}\cdot Ph_4P^+Cl^-$, $\mathbf{I_4TEPM}\cdot Ph_4P^+Br^-$ and $\mathbf{I_4TEPM}\cdot Ph_4P^+I^-$. CCDC 1582932–1582934 contain the supplementary crystallographic data. They can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures. Structural images were generated using Mercury[4] and Olex2.[5] Topological analysis was performed with ToposPro.[6]

Table S1: Crystallographic data for the cocrystals.

Code	$\mathbf{I_4TEPM}\cdot Ph_4P^+Cl^-$	$\mathbf{I_4TEPM}\cdot Ph_4P^+Br^-$	$\mathbf{I_4TEPM}\cdot Ph_4P^+I^-$
Formula moiety	$(C_{33}H_{16}I_4)$ $(C_{24}H_{20}PCl)$	$(C_{33}H_{16}I_4)$ $(C_{24}H_{20}PBr)$	$(C_{33}H_{16}I_4)$ $(C_{24}H_{20}PI)$
Empirical formula	$C_{57}H_{36}ClI_4P$	$C_{57}H_{36}BrI_4P$	$C_{57}H_{36}I_5P$
Molecular weight	1297.88	1339.34	1386.33
Color, Habit	Yellow, block	Yellow, prism	Yellow, plate
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group, Z	*I*2/*a*, 8	*I*2/*a*, 8	*I*2/*a*, 8
a, Å^3	17.3730(6)	17.4076(9)	17.4190(11)
b, Å^3	17.4497(7)	17.4445(11)	17.3989(8)
c, Å^3	33.5122(11)	34.0495(19)	34.9081(17)
α, °	90.00	90.00	90.00
β, °	90.168(4)	90.184(4)	90.638(6)
γ, °	90.00	90.00	90.00
Volume, Å^3	10159.3(6)	10339.7(10)	10579.0(10)
Density, g/cm^3	1.693	1.721	1.741
Temperature, °K	296(2)	296(2)	296(2)
Crystal size, mm (min × mid × max)	0.34 × 0.38 × 0.56	0.28 × 0.32 × 0.58	0.19 × 0.51 × 0.59
X-ray wavelength, Å	0.71073	0.71073	0.71073
μ, mm^{-1}	2.574	3.250	3.005
Absorption corr	multi-scan	multi-scan	multi-scan
Trans min / max	0.70163 / 1.000	0.607 / 1.000	0.298 / 1.000
θ_{min}, °	4.261	4.256	4.251
θ_{max}, °	27.000	27.000	27.000
Reflections			
collected	22677	23245	26629
independent	11108	11248	10852
observed	7817	7251	6446
Threshold expression	>2σ(I)	>2σ(I)	>2σ(I)
R1 (observed)	0.0571	0.0661	0.0709
wR_2 (all)	0.1620	0.1491	0.1743
Goodness of fit (all)	1.040	1.075	1.046
Δρ max / min	2.018 / -0.695	1.306 / -0.657	0.816 / -1.185
2θ limit	25.24	25.24	25.24
Completeness to 2θ limit	0.996	0.996	0.938

Table S2: Halogen bonding features of the cocrystals.

Compound	C–I···X⁻	*d*(I···X⁻)/Å	*nd*	*rr*/%	∠(C–I···X⁻)/°
I_4TEPM·$Ph_4P^+Cl^-$	C9–I1···Cl1	3.1326(14)	0.827	17.35	166.4(2)
	C17–I2···Cl1[a]	3.1734(15)	0.837	16.27	170.2(2)
	C25–I3···Cl1[b]	3.1064(14)	0.820	18.04	177.4(2)
	C33–I4···Cl1[c]	3.1137(14)	0.822	17.84	176.8(2)
I_4TEPM·$Ph_4P^+Br^-$	C9–I1···Br1	3.1984(9)	0.812	18.82	177.5(2)
	C17–I2···Br1[d]	3.2492(9)	0.825	17.53	165.7(2)
	C25–I3···Br1[e]	3.2051(10)	0.813	18.65	176.2(2)
	C33–I4···Br1[f]	3.2705(10)	0.830	16.99	170.7(3)
I_4TEPM·$Ph_4P^+I^-$	C9–I2···I1	3.3758(10)	0.808	19.24	176.6(3)
	C17–I3···I1[g]	3.4470(10)	0.825	17.54	173.1(4)
	C25–I4···I1[h]	3.4126(10)	0.816	18.36	165.8(3)
	C33–I5···I1[i]	3.3807(9)	0.809	19.12	176.3(3)

Normalized distance, $nd = d_{xy}/(r_x + r_y)$, where d_{xy} is the crystallographically determined XB distance, and r_x and r_y are the appropriate (van der Waals[7] or revised Shannon-Prewitt effective ionic[8]) radii for the two involved species, organic iodine atom and the inorganic halide ion (I = 1.98 Å, Cl^- = 1.81 Å, Br^- = 1.96 Å, I^- = 2.20 Å). Radii reduction, rr (%) = $(1 - nd) \times 100$. Symmetry transformations used to generate equivalent atoms: [a]-1/2+x,1/2+y,1/2+z. [b]-1+x,y,z. [c]-1/2+x,-1/2+y,1/2+z. [d]1+x,y,z. [e]1/2+x,1/2+y,1/2+z. [f]1/2+x,-1/2+y,1/2+z. [g]1/2+x,1/2+y,-1/2+z. [h]1+x,y,z. [i]1/2+x,-1/2+y,-1/2+z.

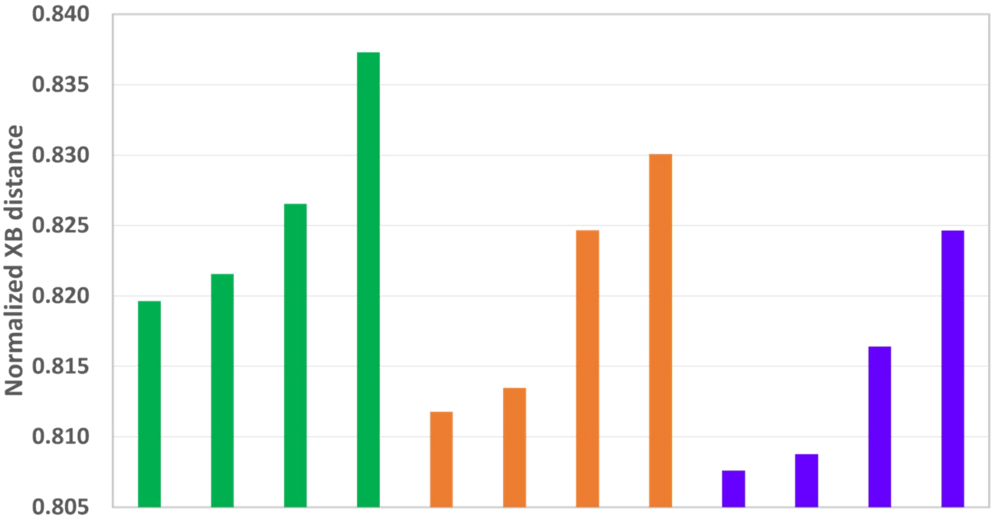


Figure S23: Varying of normalized XB lengths across the three structures (chloride - green, bromide - orange and iodide - violet).

References

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