Electronic Supplementary Information

Single source precursor routes for synthesis of PdTe nanorods and particles: solvent dependent control of shapes

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Experimental details

Physical measurements

The C, H and N analyses were carried out with a Perkin-Elmer 2400 Series II C, H and N analyzer. The ¹H, ¹³C{¹H} and ⁷⁷Se{¹H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47 and 57.24 MHz respectively. IR spectra in the range 4000-400 cm⁻¹ were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. High resolution mass spectral (HR-MS) measurements were performed with electron spray ionization (10 *eV*, 180 °C source temperature) and using sodium formate as calibrant on a Bruker MIcroTOF-Q II, taking sample in CH₃CN. The diffraction data on single crystals of **1** and **2** were collected on a Bruker AXS SMART Apex CCD diffractometer using Mo-*Ka* (0.71073 Å) radiations at 298(2) K. The software SADABS¹ was used for absorption correction (if needed) and SHELXTL for space group, structure determination and refinements.² All non–hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached. The least-square refinement cycles on *F*² were performed until the model converged. High-resolution TEM characterization revealing particle sizes and shapes was performed with a Philips Tecnai F20 operated at 200 kV. Samples for high resolution transmission electron microscopy

(HR-TEM) were prepared by drying a drop of dispersion of nano-crystals in ethanol on carboncoated copper grid. The elemental composition of NPs were studied with a Carl ZEISS EVO5O scanning electron microscope (SEM) and associated EDX system Model QuanTax 200, which is based on the SDD technology and provides an energy resolution of 127 eV at Mn-K α . Sample was mounted on a circular metallic sample holder with a sticky carbon tape. The melting points determined in an open capillary are reported as such. Yields refer to isolated yields of compounds which have purity \geq 95%.

Chemicals and reagents

4-Bromopyrazole, sodium borohydride, palladium(II) chloride procured from Sigma-Aldrich (USA) were used as received. 4–Bromo–1–(2–chloroethyl)–1H–pyrazole was prepared by the method reported earlier.³ All the solvents were dried and distilled before use by standard procedures.⁴ The common reagents and chemicals available commercially within the country were used.

Synthesis of L1

Ditelluride (0.469 g, 1.0 mmol) dissolved in 30 mL of EtOH was stirred under reflux in N₂ atmosphere. Sodium borohydride (0.076 g, 2.0 mmol) was added to it as solid so that it became colorless due to the formation of (*p*-MeOC₆H₄)TeNa. 4–Bromo–1–(2–chloroethyl)–1*H*–pyrazole (0.419 g, 2.0 mmol) dissolved in 10 mL of ethanol was added to the colorless solution with constant stirring and the mixture was further refluxed for 5 h. It was extracted with chloroform (4 × 25 mL). The extract was washed with water (3 × 40 mL) and dried over anhydrous sodium sulphate. The solvent from extract was evaporated off under reduced pressure on a rotary evaporator to get **L1** as yellow oil.

Yield: 0.718 g, 88%. ¹H NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 3.15 (t, ${}^{3}J_{H-H} = 7.199$ Hz, 2H, H₅), 3.80 (s, 3H, OCH₃), 4.38 (t, 2H, ${}^{3}J_{H-H} = 7.20$ Hz, H₆), 6.73-7.78 (m, 2H, H₂), 7.35 (s, 1H, H₇), 7.40 (s, 1H, H₉), 7.66-7.68 (m, 2H, H₃). ¹³C{¹H} NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 6.9 (C₅), 54.6 (C₆), 55.2 (OCH₃), 92.8 (C₈), 99.4 (C₁), 115.40 (C₂), 129.0 (C₇), 140.0 (C₉), 141.4 (C₃), 160.15 (C₄). ¹²⁵Te{¹H} NMR (CDCl₃, 25 °C vs Me₂Te): δ (ppm). 457.1. HR-MS (CH₃CN) [M + Na]⁺ (*m/z*) = 432.9148; calculated value for [C₁₂H₁₃BrN₂NaOTe]⁺ = 432.9157 (δ: 2.2 ppm). IR (KBr, cm⁻¹): 2929 (m; *v*_{C-H aromatic}), 2843 (s; *v*_{C-H aliphatic}), 1580 (s; *v*_{C=N aromatic}), 1485 (s; *v*_{C=C aromatic}), 1288 (m; *v*_{C-N aliphatic}), 817 (m; *v*_{C-H aromatic}).

Synthesis of L2

Tellurium powder (0.127 g, 1.0 mmol) added in 30 mL of ethanol were stirred under reflux in N₂ atmosphere. Solid sodium borohydride (0.074 g, 2.0 mmol) was added to it so that it became colourless. 4–Bromo–1–(2–chloroethyl)–1*H*–pyrazole (0.418 g, 2.0 mmol) dissolved in 10 mL of ethanol was added with constant stirring and the mixture stirred with refluxing further for 5 h. It was extracted with chloroform (4 × 25 mL). The extract was washed with water (3 × 40 mL) and dried over anhydrous sodium sulphate. The solvent was evaporated off under reduced pressure on a rotary evaporator to get **L2** as yellow oil.

Yield: 0.404 g, 85%. ¹H NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 2.92 (t, ³*J*_{H-H} = 7.2 Hz, 4H, H₅), 4.37 (t, ³*J*_{H-H} = 7.2 Hz, 4H, H₄), 7.43 (s, 2H, H₃), 7.47 (s, 2H, H₁). ¹³C{¹H} NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 2.3 (C₅), 54.8 (C₄), 92.9 (C₂), 129.3 (C₃), 140.1 (C₁). ¹²⁵Te{¹H} NMR (CDCl₃, 25 °C vs Me₂Te): δ (ppm). 238.6. HR-MS (CH₃CN) [M + Na]⁺ (*m/z*) = 498.8347; calculated value for [C₁₀H₁₂Br₂N₄NaTe]⁺ = 498.8384 (δ : 7.6 ppm). IR (KBr, cm⁻¹): 2924 (m; *v*_{C-H aromatic}), 2857 (s; *v*_{C-H aliphatic}), 1595 (s; *v*_{C=N aromatic}), 1445 (s; *v*_{C=C aromatic}), 1299 (m; *v*_{C-N aliphatic}), 800 (m; *v*_{C-H aromatic}).

Synthesis of [Pd(L1)Cl₂] complex (1)

Solid $[Pd(CH_3CN)_2Cl_2]$ (0.052 g, 0.2 mmol) taken in CH_3CN (20 mL) was stirred under reflux until a clear light yellow colored solution was obtained. The L1 (0.082 g, 0.2 mmol) dissolved in CH_3CN (5 mL) was added. The reaction mixture was further refluxed for 5 h. It was cooled thereafter to room temperature, concentrated upto 7 mL on a rotary evaporator and mixed with diethyl ether (10 mL). The complex 1 resulting as orange colored solid was filtered, washed with diethyl ether (10 mL) and dried in *vacuo*. Single crystals of 1 were grown by slow evaporation of its solution in DMSO.

Yield: 0.108 g, 92%. Anal. Calcd for C₁₂H₁₃BrCl₂N₂OPdTe: C, 24.59; H, 2.24; N, 4.78. Found: C, 24.67; H, 2.06; N, 5.40. Mp 190.0 °C. ¹H NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 2.61 (bs, 1H, H₅), 2.97-3.03 (m, 1H, H₅), 3.31 (s, 3H, OCH₃), 4.77-4.84 (m, 1H, H₆), 5.01-5.04 (m, 1H, H₆), 4.77-4.88 (m, 1H, H₆), 5.01-5.04 (m, 1H, H₆), 6.97-6.99 (m, 2H, H₂), 7.86-7.88 (m, 2H, H₃), 8.10 (s, 1H, H₇), 8.33 (s, 1H, H₉). ¹³C{¹H} NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 18.3 (C₅), 52.7 (C₆), 55.2 (OCH₃), 92.4 (C₈), 109.0 (C₁), 115.4 (C₂), 135.2 (C₇), 137.8 (C₃), 144.0 (C₉), 160.6 (C₄). ¹²⁵Te{¹H} NMR (CDCl₃, 25 °C vs Me₂Te): δ (ppm). 683.9. HR-MS (CH₃CN) [M – Cl]⁺ (*m*/*z*) = 550.7967; calulated value for [C₁₂H₁₃BrClN₂PdTe]⁺ = 550.7989 (δ: 3.9 ppm). IR (KBr, cm⁻¹): 3113 (m; v_{C-H aromatic}), 2992 (s; v_{C-H aliphatic}), 1578 (s; v_{C=N aromatic}), 1488 (m; v_{C=C aromatic}), 1295 (m; v_{C-N aliphatic}), 819 (m; v_{C-H aromatic}).

Synthesis of [Pd(L2)Cl]BF₄ complex (2)

Solid $[Pd(CH_3CN)_2Cl_2]$ (0.052 g, 0.2 mmol) taken in CH₃CN (20 mL) was stirred under reflux until a clear light yellow colored solution was obtained. The solution of ligand L2 (0.095 g, 0.2 mmol) dissolved in CH₃CN (5 mL) was added. The reaction mixture was further refluxed for 5 h. Thereafter solid AgBF₄ (0.038 g, 0.2 mmol) was added and the mixture refluxed further for 2 h. It was cooled to room temperature and precipitated AgCl was filtered off through celite. The filtrate was concentrated to 5 mL on a rotary evaporated and mixed with diethyl ether (10 mL) to obtain 2 as yellow solid, which was filtered and dried in *vacuo*. The single crystals of 2 were grown by slow evaporation of its solution in CH₃CN.

Yield: 0.591 g, 84%. Anal. Calcd for $C_{10}H_{12}BBr_2ClF_4N_4PdTe: C, 17.05; H, 1.72; N, 7.95.$ Found: C, 17.92; H, 1.67; N, 8.63. Mp 170.0 °C. ¹H NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 2.85-2.92 (m, 2H, H₅), 3.28-3.32 (m, 2H, H₅), 5.21-5.32 (m, 2H, H₄), 5.40-5.45 (m, 2H, H₄), 7.97 (s, 2H, H₃), 8.37 (s, 2H, H₁). ¹³C{¹H} NMR (CDCl₃, 25 °C vs Me₄Si): δ (ppm) 17.8 (C₅), 55.7 (C₄), 93.1 (C₈), 135.8 (C₃), 144.0 (C₁). ¹²⁵Te{¹H} NMR (CDCl₃, 25 °C vs Me₂Te): δ (ppm). 697.9. HR-MS (CH₃CN) [M - BF₄]⁺ (*m*/*z*) = 616.7175; calulated value for [C₁₀H₁₂Br₂ClN₄PdTe]⁺ = 616.7193 (δ : 3.0 ppm).IR (KBr, cm⁻¹): 3123 (m; *v*_{C-H aromatic}), 2923 (s; *v*_{C-H aliphatic}), 1641 (s; *v*_{C=N aromatic}), 1446 (m; *v*_{C=C aromatic}), 1303 (m; *v*_{C-N aliphatic}), 844 (m; *v*_{C-H aromatic}).

Synthesis of PdTe nano-structures

(a) Thermolysis of 1 and 2 in OA-ODE

A mixture of OA-ODE (3 mL/3 mL) and 1/2 (0.586/0.704 g, 1.0 mmol) was heated to 220 °C under N₂ atmosphere in a three neck flask for 2 h with continuous stirring. The colour of the mixture changed from dark red to red-brown within 30 min and brown-black precipitate started appearing thereafter. The mixture was cooled to room temperature and 20 mL of acetone was added into the flask to obtain a brown-black precipitate which was separated by centrifugation. The precipitate was washed three times with methanol (20 mL) and dried in vacuo.

(b) Thermolysis of 1 and 2 in TOP

A mixture of TOP (3 mL/3 mL) and 1/2 (0.586/0.704 g, 1.0 mmol) was heated to 220 °C under N₂ atmosphere in a three neck flask for 2 h with continuous stirring. The colour of the mixture changed from dark red to red-brown within 30 min and brown-black precipitate started appearing thereafter. The mixture was cooled to room temperature and 20 mL of acetone was added into the flask to obtain a brown-black precipitate which was separated by centrifugation. The precipitate was washed three times with methanol (20 mL) and dried in vacuo.

Solubility of ligands and complexes in common solvents

The yellow solids **1** and **2** were found air stable and thermally robust. The ligands **L1**, **L2** were found soluble in common organic solvents. The complex **1** shows good solubility in DMF and DMSO. It has been found sparingly soluble in CH_3CN , CH_2Cl_2 and $CHCl_3$. In CH_3OH , diethyl ether, THF and hexane it has negligible solubility. On the other hand complex **2** has been found soluble in DMF, DMSO and CH_3CN , sparingly soluble in CH_2Cl_2 , and $CHCl_3$ and insoluble in diethyl ether, hexane and CH_3OH .



TEM images of PdTe nanostructures and their stability against aggregation over time

Figure S1. TEM Images of freshly prepared nanostructures

TEM images of freshly prepared PdTe nanostructures (nanorod and hexagonal nanoparticles) are shown in Figure S1. To understand the stability of nanoparticles with time, TEM images were taken after two months of their preparation and shown in Figure S2. The nanostructures (nanorod and hexagonal nanoparticles) show slight aggregation as compared to that of freshly prepared sample. Thus their instability is not much.



Figure S2. TEM images of PdTe nanostructures after two months



Figure S3. Size distribution curve of PdTe hexagonal nanoparticles and nanorod.

Compounds	1	2
Empirical formula	C ₁₂ H ₁₃ BrCl ₂ N ₂ OPdTe	$C_{10}H_{12}Br_2ClN_4PdTe$. BF_4
Formula wt.	586.04	704.30
Crystal size [mm]	0.35×0.23×0.22	0.35×0.25×0.21
Crystal system	Triclinic	Monoclinic
Space group	P-1	<i>P 21/c</i>
Unit Cell	a = 8.2495(14)Å	a = 15.213(6)
dimension	b = 10.2881(18)	b = 11.222(5)
	c = 10.6749(18)	c = 11.102(5)
	$\alpha = 75.921(3)^{\circ}$	$\alpha = 90.00$
	$\beta = 68.737(3)^{\circ}$	$\beta = 102.930(7)$
	$\gamma = 88.690(3)^{\circ}$	$\gamma = 90.00$
Volume [Å ³]	816.8(2)	1847.1(13)
Ζ	2	4
Density (Calc.) [Mg ^{-m⁻³}]	2.383	2.552
Absorption coeff. [mm ⁻¹]	5.655	7.061
<i>F</i> (000)	548.0	1304.0
θ range [°]	2.55-28.07	2.34–24.18
Index ranges	$-9 \le h \le 9$	$-18 \le h \le 18$
	$-12 \le k \le 12$	$-13 \le k \le 13$
	$-12 \le l \le 12$	$-13 \le l \le 13$
Reflections collected	7657	17275
Independent reflections $(R_{int.})$	2839 (0.0370)	3251(0.0429)
Max./min. Transmission	0.291/0.226	0.082/0.035
Data/restraints/parameters	2839/0/182	3251/0/217
Goodness-of-fit on F^2	1.041	1.117
Final R indices	$R_1 = 0.0380,$	$R_1 = 0.0832$
$[I \ge 2\sigma(I)]$	$wR_2 = 0.0980$	$wR_2 = 0.1023$
R indices (all data)	$R_1 = 0.0421,$	$R_1 = 0.0518$
	$wR_2 = 0.1005$	$wR_2 = 0.1065$
Largest diff. peak/hole [e.Å ⁻³]	1.778/-1.178	0.576/-0.688

Table S1. Crystal data and structural refinement parameters

Compounds	Bond length [Å]		Bond angle [^o]	
1	Pd(1)—Te(1)	2.5116(6)	Cl(1)—Pd(1)—Te(1)	82.02(4)
	Pd(1)—N(2)	2.036(4)	Cl(2)—Pd(1)—Te(1)	175.70(3)
	Pd(1)—Cl(1)	2.3012(14)	N(2)—Pd(1)—Te(1)	92.81(12)
	Pd(1)—Cl(2)	2.3938(13)	N(2) - Pd(1) - Cl(1)	169.88(12)
	Te(1)—C(6)	2.122(5)	N(2) - Pd(1) - Cl(2)	90.66(12)
	Te(1)—C(7)	2.144(5)	Cl(2)— $Pd(1)$ — $Cl(1)$	94.16(5)
	N(1)—N(2)	1.361(5)	C(6)—Te(1)—Pd(1)	96.64(14)
	N(1)—C(8)	1.450(6)	C(7)—Te(1)—Pd(1)	101.16(15)
	N(1)—C(9)	1.342(6)	C(11)—N(2)—Pd(1)	123.9(3)
	N(2)—C(11)	1.340(6)	N(1)—N(2)—Pd(1)	129.3(3)
	Br(1)—C(10)	1.869(5)	C(9)—C(10)—Br(1)	127.8(4)
			C(11)—C(10)—Br(1)	125.9(4)
2	Pd(1)—N(2)	1.993(5)	N(2)-Pd(1)-Te(1)	90.26(16)
	Pd(1)—N(4)	2.014(6)	N(4)-Pd(1)-Te(1)	91.33(17)
	Pd(1)—Te(1)	2.5313(10)	Te(1)-Pd(1)-Cl(1)	177.51(6)
	Pd(1)—Cl(1)	2.3236(19)	N(2)–Pd(1)–Cl(1)	89.26(16)
	Te(1)—C(5)	2.157(8)	N(4)-Pd(1)-Cl(1)	89.26(17)
	Te(1)—C(6)	2.142(7)	N(2)-Pd(1)-N(4)	177.0(2)
	N(1)—C(3)	1.328(9)	C(5)–Te(1)–Pd(1)	97.2(2)
	N(1)—C(4)	1.465(9)	C(6)–Te(1)–Pd(1)	96.5(2)
	N(2)—C(1)	1.331(9)	C(1)–N(2)–Pd(1)	127.4(5)
	N(3)—C(7)	1.455(9)	N(1)–N(2)–Pd(1)	126.1(4)
	N(3)—C(8)	1.326(10)	C(10)–N(4)–Pd(1)	128.3(5)
	N(4)—C(10)	1.335(9)	N(3)–N(4)–Pd(1)	123.2(4)
	N(1)—N(2)	1.359(8)	C(1)—C(2)—Br(1)	124.8(6)
	N(3)—N(4)	1.363(8)	C(3)—C(2)—Br(1)	128.7(6)
	Br(1)—C(2)	1.868(7)		
	Br(2)—C(9)	1.864(7)		

Table S2. Selected bond lengths [Å] and bond angles [°]

1		2			
Cl(1)…H(7A)	2.769(2)	B(1) - F(1) - H(5A)	2.373(12)		
(Inter-molecular)		(inter-molecular)			
Cl(2)…H(8B)	2.772(4)	B(1)—F(2)····H(6B)	2.466(14)		
(Inter-molecular)		(inter-molecular)			
Cl(1)…H(8A)	2.706(5)	B(1)—F(3)····H(4B)	2.671(11)		
(Inter-molecular)		(inter-molecular)			
Cl(2)…H(8A)	2.728(4)	B(1)—F(3)····H(3)	2.523(10)		
(Inter-molecular)		(inter-molecular)			
С(12)—Н(12С)…π	2.937(4)	B(1)—F(3)····H(8)	2.781(12)		
		(inter-molecular)			
		B(1)—F(4)···H(7A)	2.480(9)		
		(inter-molecular)			
		B(1)—F(1)···H(6A)	2.486(13)		
		(inter-molecular)			

 $\label{eq:states} Table \ S3. \ Distances \ [\text{\AA}] \ of \ inter \ and \ intra-molecular \ interactions \ for \ complexes \ 1 \ and \ 2.$



Figure S4. Inter-molecular C–H···Cl and C–H··· π interactions in complex 1



Figure S5. Inter-molecular C–H…F interactions in complex 2

NMR Spectra of ligands and complexes



Figure S6. ¹H NMR of Ligand (L1)



Figure S7. $^{13}C{^{1}H}$ NMR of Ligand, L1







Figure S9. $^{13}C{^{1}H}$ NMR of Ligand, L2







Figure S11. ${}^{13}C{}^{1}H$ NMR of Complex 1







Figure S14. 125 Te $\{^{1}$ H $\}$ NMR of Ligand, L1



Figure S15. 125 Te $\{^{1}$ H $\}$ NMR of Ligand, L2









Figure S17. 125 Te $\{^{1}$ H $\}$ NMR of Complex, 2

HR-MS Spectra of Ligands and Complexes

•		Mass	Spectru	ım Sm	nartForn	nula I	Repor	t			
Analysis Info						Acqu	isition Dat	e 5/24/3	2013 12	2:18:02 F	РМ
Analysis Name D:\Data\MAY_13\KK-1A.d Method tune_low.m Sample Name 1 Comment		A.d			Operator Instrument / Ser#		Sharr er# micrC	Sharma/Singh micrOTOF-Q II 10262			
Acquisition Para	ameter										
Source Type ESI Focus Not acti Scan Begin 50 m/z Scan End 1500 m	active n/z 0 m/z	lon Polarity Set Capillary Set End Plate Offset Set Collision Cell RF		Positive 4500 V -500 V 100.0 Vpp	Set Nebulizer Set Dry Heater Set Dry Gas Set Divert Valve		0.3 Bar 180 °C 4.0 l/min Source				
		360.3210	9415								
	242.2	832	573.24	86 		101	7.8756				
Meas. m/	/z. #	Formula		Score	m/z	err [ppm]	Mean err [ppm]	mSigm a	rdb	e [—] Conf	N-R ule
432.915	57 1	C 12 H 13 Br N	2 Na O Te	100.00	432.9148	-2.2	-23.1	352.5	6.5	even	ok

Figure S18. Mass Spectra of Ligand L1



Figure S19. Mass Spectra of Ligand L2



Figure S20. Mass Spectra of Complex 1







Figure S22. SEM-EDX of PdTe Nano-particles obtained by thermolysis of 1 in OA-ODE



Figure S23. SEM-EDX of PdTe Nano-particles obtained by thermolysis of 2 in OA-ODE



Figure S24. SEM-EDX of PdTe Nano-particles obtained by thermolysis of 1 in TOP



Figure S25. SEM-EDX of PdTe Nano-particles obtained by thermolysis of 2 in TOP

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