Supporting Information for

Glacial Acetic Acid as Resolution Solvent for Growing Enantiopure Crystals from Racemic Mixtures

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Experimental Section

Reagents.

Bis(diphenylphosphino)methane (dppm, purity 98%), *t*-butylisonitrile (CN^{t}Bu, purity 97%), hexamethyldisilathiane [$(Me_3Si)_2S$, purity 98%] and palladium acetate [$Pd(OAc)_2$, purity 99%] were purchased from Energy Chemical (Shanghai, China). (*S*)-1,1'-Binaphthyl-2,2'-diyl hydrogen phosphate and (*R*)-1,1'-Binaphthyl-2,2'-diyl hydrogen phosphate (***S*-Phos** and ***R*-Phos**, purity 99%) were purchased from Bidepharm (Shanghai, China). Potassium hexafluorophosphate (KPF_6, purity 99%) was purchased from Innochem (Beijing, China). Acetic acid (CH_3COOH, A.R.), dichloromethane (CH_2Cl_2, A.R.), methanol (CH_3OH, A.R.) and diethyl ether (Et_2O, A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Carbon monoxide (CO, purity 99.999%) was purchased from Messer (Foshan, China). All reagents were used as received without further purification.

Synthesis of $[Pd_4(CO)_4(OAc)_4]$.

The $[Pd_4(CO)_4(OAc)_4]$ was synthesized according to the modified literature procedure[1]. In brief, 20 mg $Pd(OAc)_2$ was dissolved in 6 mL acetic acid. The mixture was stirred under 2 atm CO at 60 °C for 2 hours, then kept under CO atmosphere for another 2 hours without heating to precipitate $[Pd_4(CO)_4(OAc)_4]$ from the solution. The yellow precipitate was collected by centrifugation and used for the next step immediately without drying. The yield of $[Pd_4(CO)_4(OAc)_4]$ was ca. 90%.

Synthesis of $[Pd_4S_2(dppm)_3(CN^tBu)_2]^{2+}$ (abbreviated as Pd_4S_2).

The freshly prepared $[Pd_4(CO)_4(OAc)_4]$ was dispersed in 4 mL CH_2Cl_2 and treated with 30 μL CN^{t}Bu quickly, the yellow cloudy liquid turned colorless and transparent. 34.2 mg of dppm dissolved in 4 mL CH_2Cl_2 was added. The solution turned orange. Then 18.7 μL of $(Me_3Si)_2S$ was added into the solution and stirred 1.5 hours in air. The insoluble impurities were removed by centrifugation. The solution was subjected to the diffusion of ether. Red crystals were obtained in the yield of 62.5 % (based on $Pd(OAc)_2$) after a week.

Recrystallization of Pd_4S_2.

1 mg of **Pd_4S_2** crystals grown from dichloromethane was dissolved in 2 mL MeOH or glacial acetic acid and the solution was subjected to the diffusion of ether. PF_6^- was introduced by using KPF_6 when recrystallization solvent is MeOH. Yellow crystals were obtained after about one week.

Enantioseparation of Pd_4S_2.

3 mg of **Pd_4S_2** crystals grown from dichloromethane was dissolved in 1 mL MeOH and treated with 1 equiv. ***S*-Phos** or ***R*-Phos** then stirred for 3 hours in air. The solution was subjected to the diffusion of ether. Yellow crystals were obtained after two week.

Racemization Experiment.

***S*-Phos&*R*-Pd_4S_2** or ***R*-Phos&*S*-Pd_4S_2** dissolved in glycol as stock solution. Constant concentration solutions were prepared for racemization at 353, 358, 363 and 368K. They were placed in a cuvette with a 0.5 cm optical path and sealed with a plastic stopper and parafilm to minimize solvent evaporation. Each sample is equilibrated for two minutes at the designated temperature before recording the ECD signal. The CD signal at 444nm was recorded over the course of 30 min with intervals of 5 s.

Single crystal analysis.

The diffraction data of were collected by X-ray single crystal diffractometer with Cu Kα radiation (λ =1.54184 Å) at 100 K on an Rigaku XtaLab Synergy R system. The data were processed using CrysAlis^{Pro}[2]. Crystal structures were solved and refined using Full-matrix least-squares based on F^2 with program ShelXT[3] and ShelXL[4] within Olex2[5]. The electron densities of highly disordered molecules were treated by SQUEEZE[6] on the PLATON[7] platform.

Physical Measurements.

Electrospray ionization mass spectra (ESI-MS) were collected on Agilent 6224 time-of-flight mass spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 Spectrophotometer. ECD spectra were recorded on a JASCO J-810 CD-spectrometer. The PXRD experiment was conducted on Rigaku Ultima IV. Fourier transform infrared (FT-IR) spectrum was recorded on a Nicolet iS50 spectrophotometer. The X-ray photoelectron spectroscopic (XPS) analysis was performed on Thermo Scientific ESCALAB Xi+.

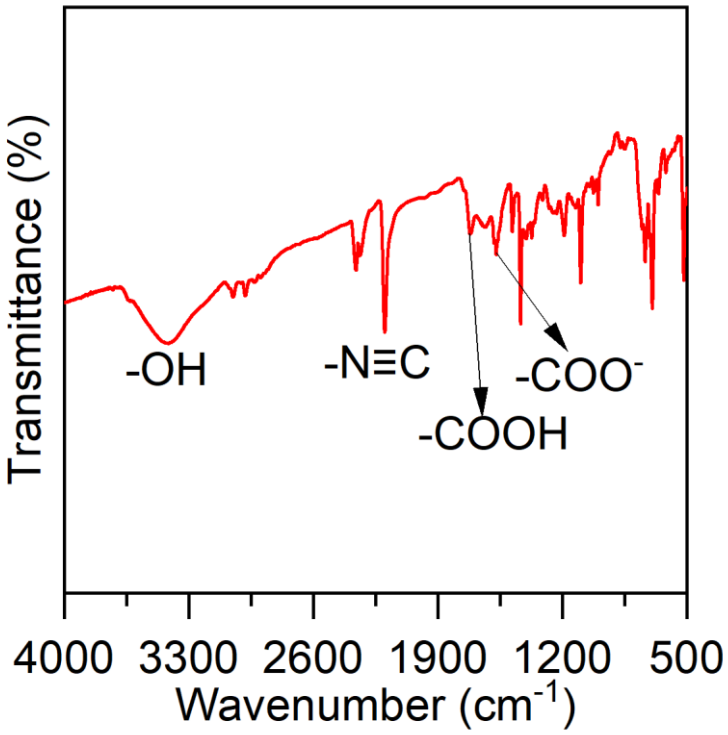

Fig. S1 The Fourier transform infrared (FT-IR) spectrum of **Pd_4S_2**.

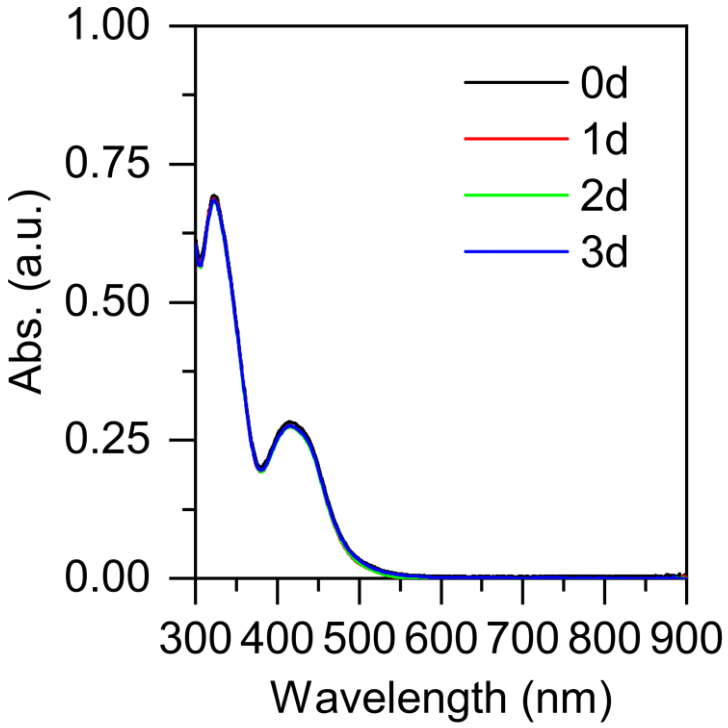

Fig. S2 UV-vis spectra of a solution of **Pd_4S_2** in methanol under ambient condition for 0-3 days showing high stability.

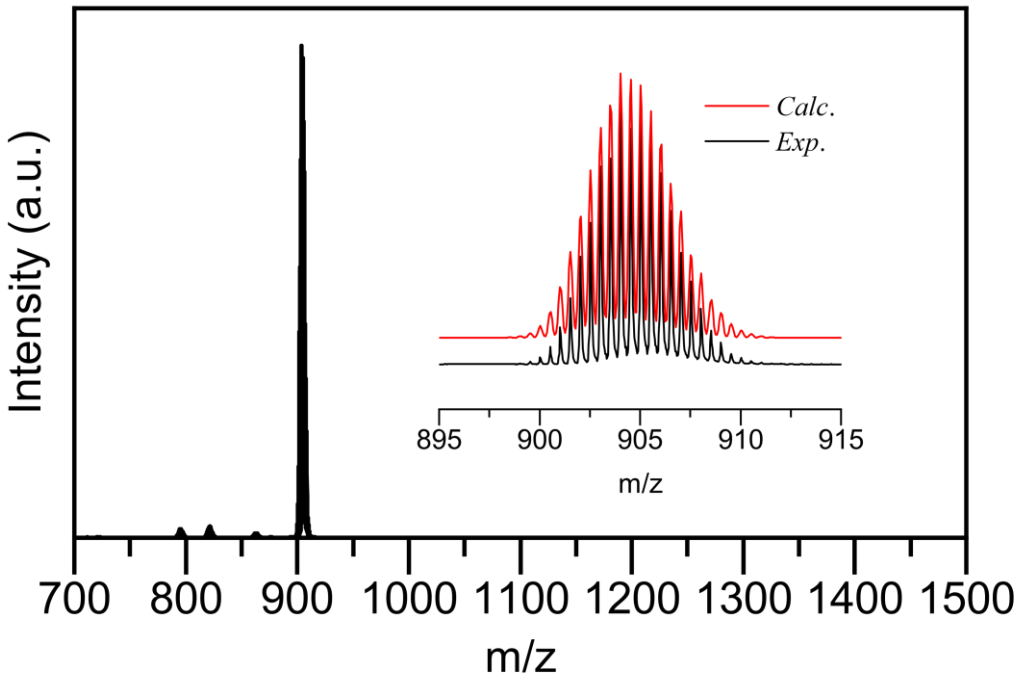

Fig. S3 ESI-MS spectrum of **Pd_4S_2**. Inset: experimental (black curve) and simulated (red curve) isotope distribution pattern of **Pd_4S_2**.

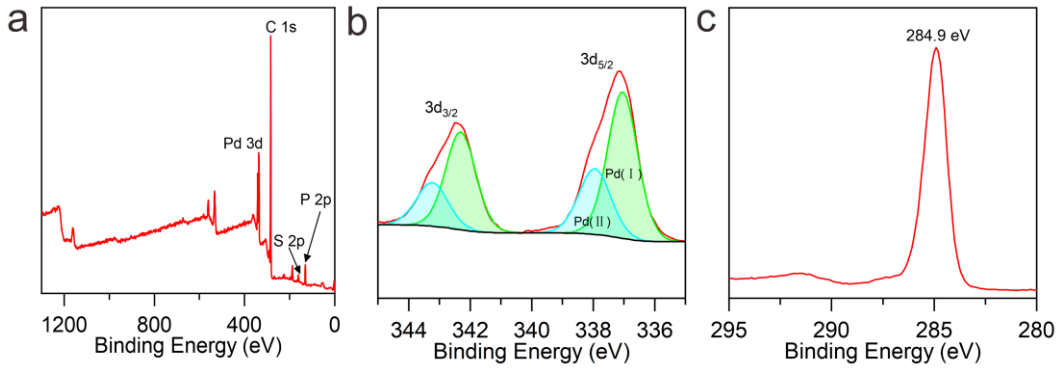

Fig. S4 The XPS spectra of ground powder of as-grown single crystals of **Pd_4S_2** grown from dichloromethane: (a) Survey spectrum. (b) High-resolution XPS spectrum of Pd 3d, which can be deconvoluted into four peaks, corresponding to the Pd(I) and Pd(II). The bonding energy (Pd $3d_{5/2}$) of fitted Pd(I) component is 337.0 eV with FWHM of 1.15 eV. The bonding energy (Pd $3d_{5/2}$) of fitted Pd(II) component is 337.9 eV with FWHM of 1.21 eV. (c) High-esolution XPS spectrum of C 1s.

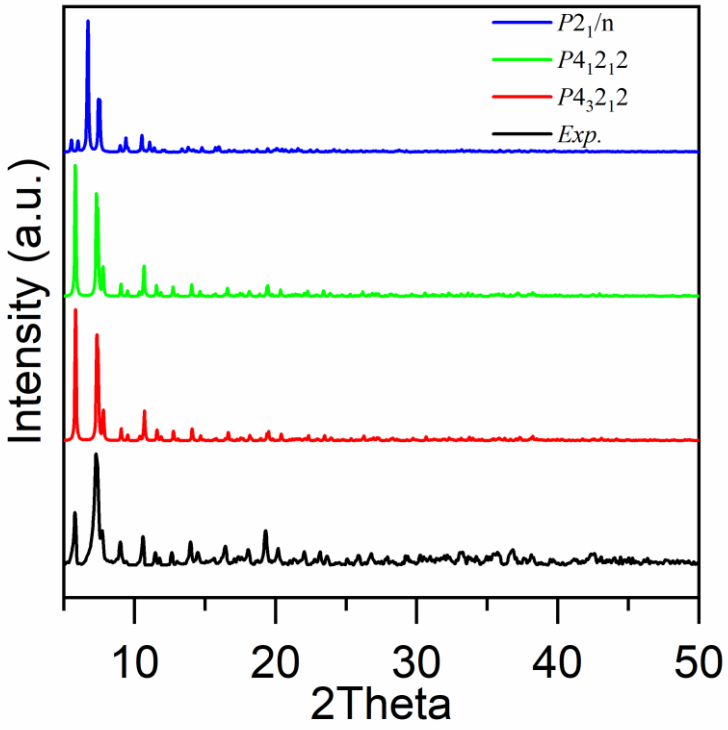

Fig. S5 Simulated (blue, green and red curves) PXRD patterns of **Pd_4S_2** under different space group based on the respective single crystal structures and experimental (black curve) PXRD pattern of **Pd_4S_2** from ground powder of as-prepared crystals grown from dichloromethane.

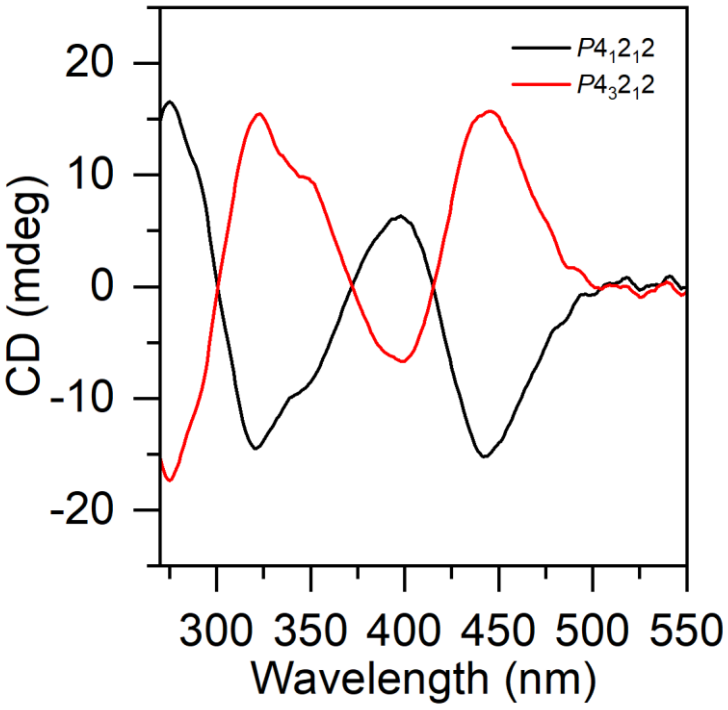

Fig. S6 The ECD spectra of single crystals of **Pd_4S_2-*P*4_12_12** and **Pd_4S_2-*P*4_32_12** dissolved in methanol.

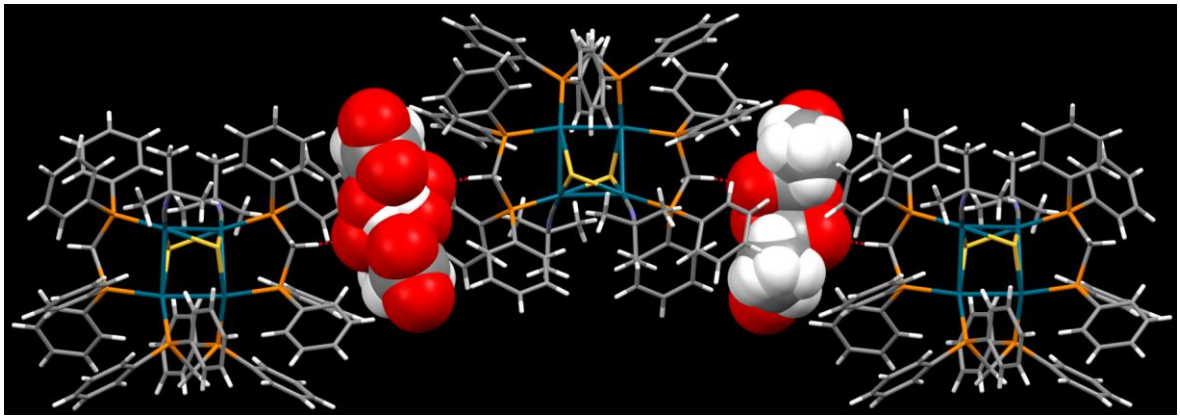

Fig. S7 The homochiral "**Pd_4S_2** chain" formed by aggregate **B** as a "linker" . Color legend: deep sky-blue, Pd; yellow, S; Orange, P; light purple, N; red, O; grey sphere, C.

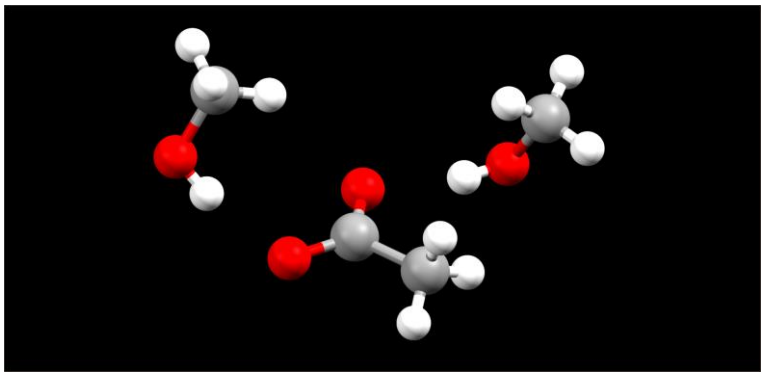

Fig. S8 The aggregate formed by methanol and acetate through hydrogen bonding in **Pd_4S_2-*P*2$_1$/*n*-MeOH**. Color legend: red, O; grey, C; white, H.

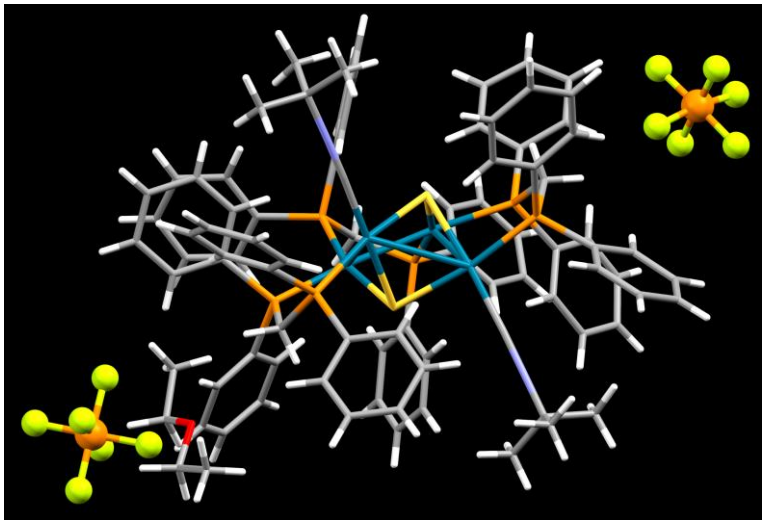

Fig. S9 Crystal structure of **Pd_4S_2** with PF_6^- as counterions. Color legend: deep sky-blue, Pd; yellow, S; Orange, P; green, F; red, O; light purple, N; grey, C; white, H.

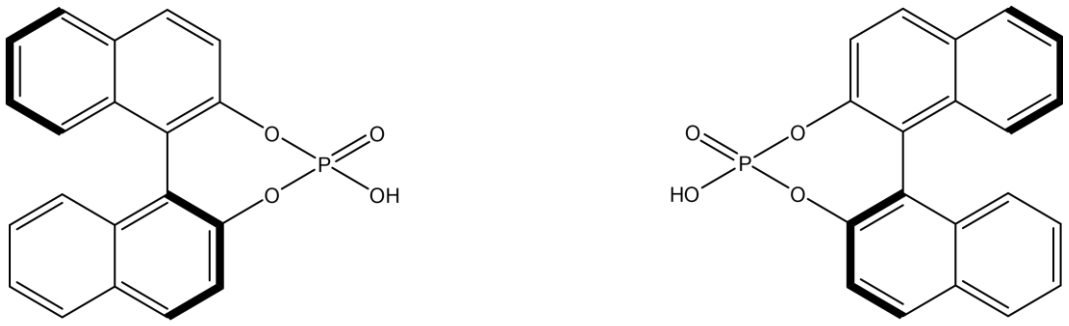

Fig. S10 Molecular structures of (*S*)-1,1'-Binaphthyl-2,2'-diyl hydrogen phosphate and (*R*)-1,1'-Binaphthyl-2,2'-diyl hydrogen phosphate.

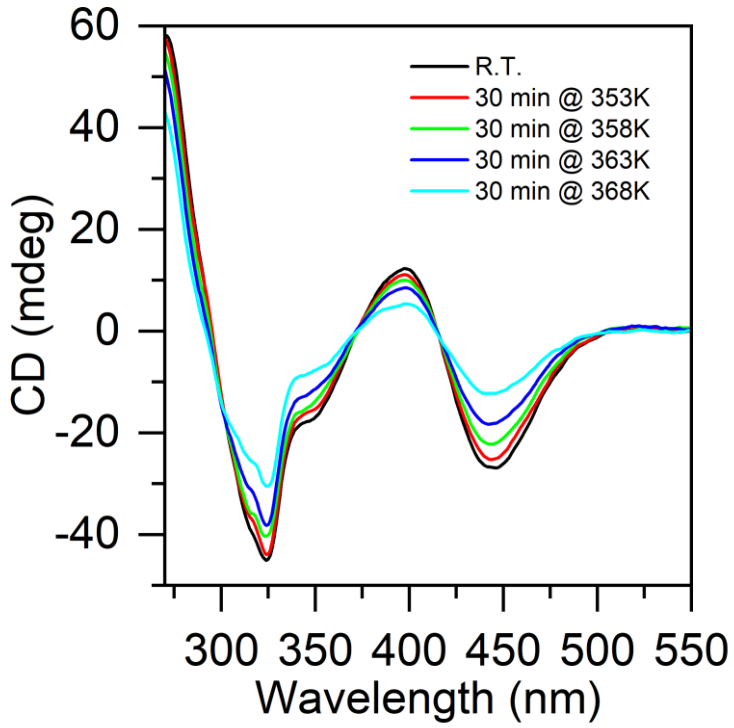

Fig. S11 The ECD spectra of ***S*-Phos&*R*-Pd_4S_2** before (black) and after thermal treatments (30 min each).

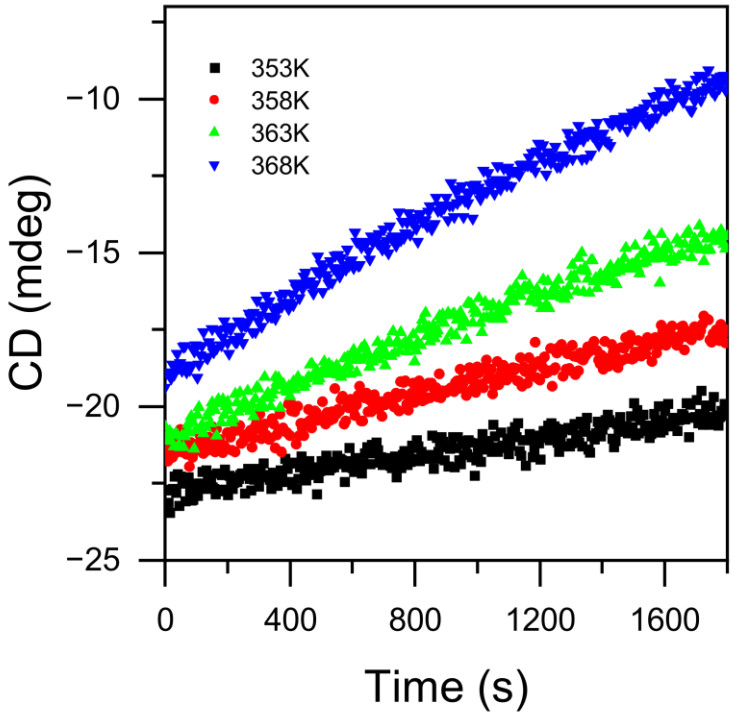

Fig. S12 ECD response at 444 nm of ***S*-Phos&*R*-Pd_4S_2** as a function of time at different temperatures.

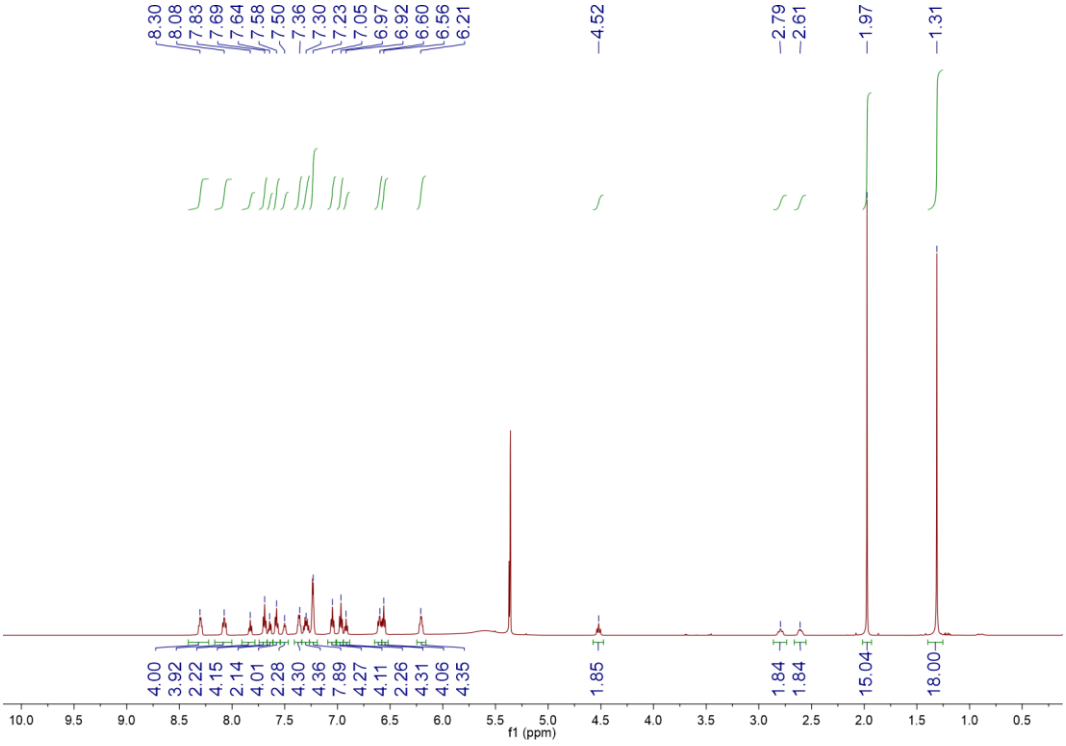

Fig. S13 ^{1}H NMR spectrum of **Pd_4S_2-*P*4$_1$2$_1$2** and **Pd_4S_2-*P*4$_3$2$_1$2** crystals in CD_2Cl_2. The peak at 1.31 ppm is assigned to the six methyl groups of the CN^tBu ligand on **Pd_4S_2** with integral area of 18. The peak at 1.97 ppm is assigned to the methyl of HOAc or OAc^-. Given the charge of **Pd_4S_2**, it's reasonale to consider the peak at 1.97 ppm as two OAc^- and three HOAc.

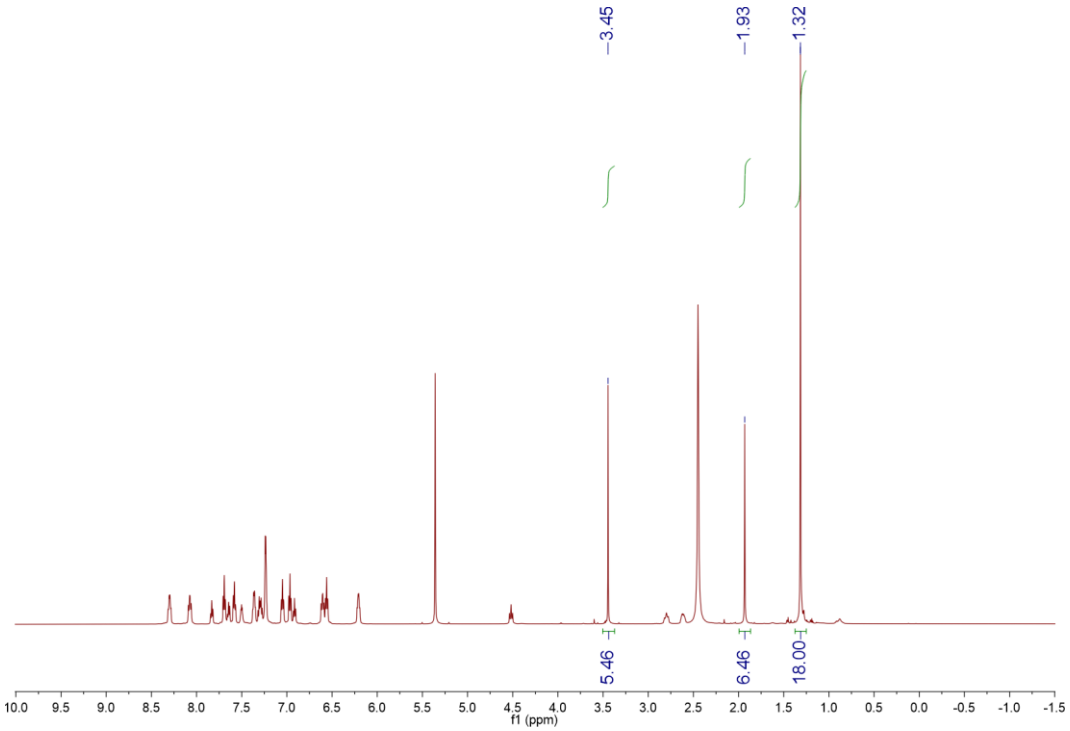

Fig. S14 ^{1}H NMR spectrum of **Pd$_4$S$_2$-*P*2$_1$/*n*-MeOH** crystals in CD_2Cl_2. The peak at 1.32 ppm is assigned to the six methyl groups of the CN^{t}Bu ligand on **Pd$_4$S$_2$** with integral area of 18. The peak at 1.93 ppm is mainly assigned to the methyl of OAc^- (Two OAc^-). The peak at 3.45 ppm is assigned to the methyl of methanol (Approximately two methanol).

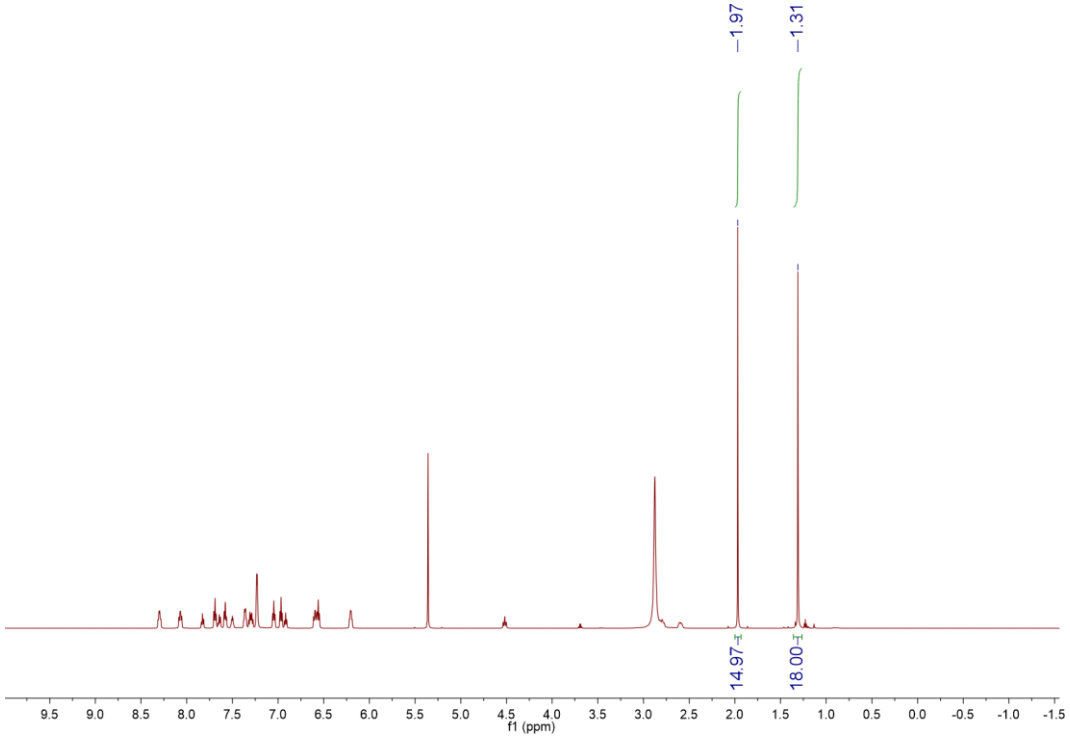

Fig. S15 ^{1}H NMR spectrum of **Pd$_4$S$_2$-*P*4$_1$2$_1$2/*P*4$_3$2$_1$2-twin** crystals in CD_2Cl_2. The peak at 1.31 ppm is assigned to the six methyl groups of the CN^{t}Bu ligand on **Pd$_4$S$_2$** with integral area of 18. The peak at 1.97 ppm is assigned to the methyl of three HOAc and two OAc^-, the same situation in **Fig. S13**.

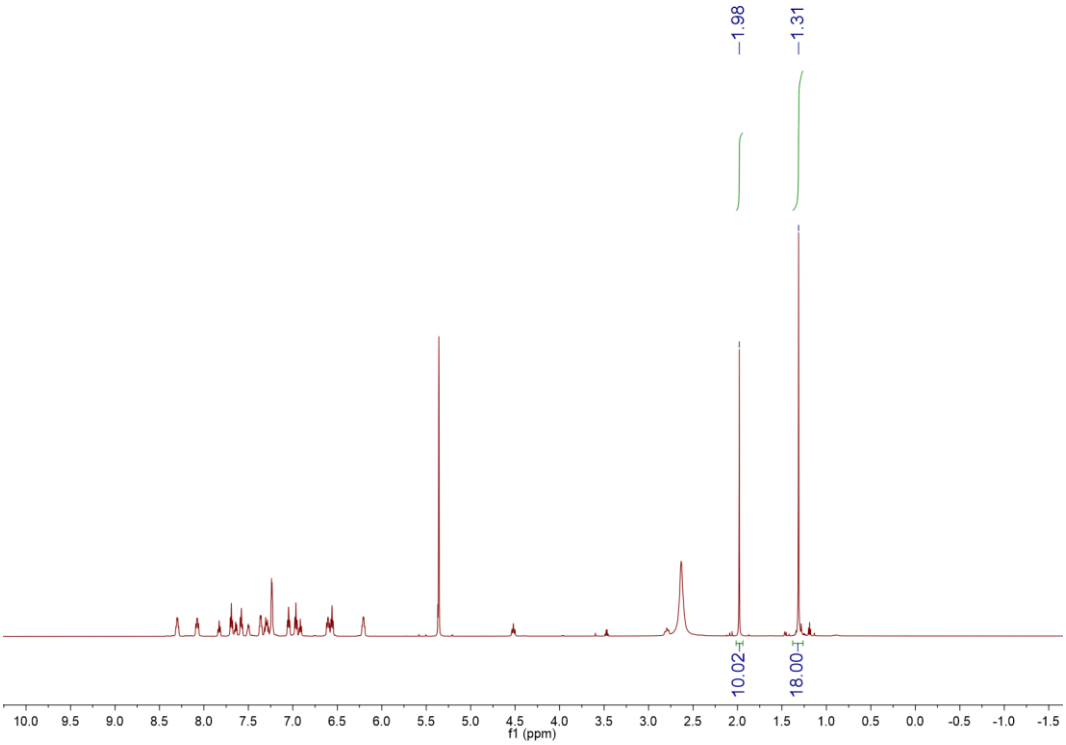

Fig. S16 ^{1}H NMR spectrum of **Pd_4S_2-*P*2$_1$/*n*** crystals in CD_2Cl_2. The peak at 1.31 ppm is assigned to the six methyl groups of the CN^{t}Bu ligand on **Pd_4S_2** with integral area of 18. The peak at 1.98 ppm is assigned to the methyl of HOAc or OAc^-. Given the charge of **Pd_4S_2**, it's reasonale to consider the peak at 1.97 ppm as two OAc^- and approximately one HOAc.

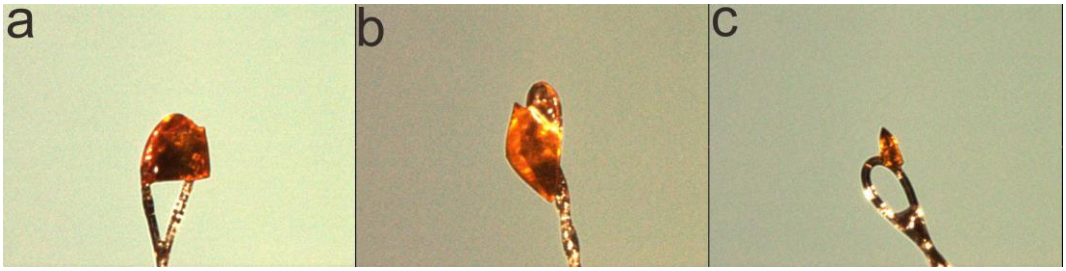

Fig. S17 Photographs of single crystals of **Pd_4S_2**. (a) Achiral space group *P*2$_1$/*n*; (b) Chiral space group with Flack parameter of 0.5; (c) Chiral space group with Flack parameter of zero.

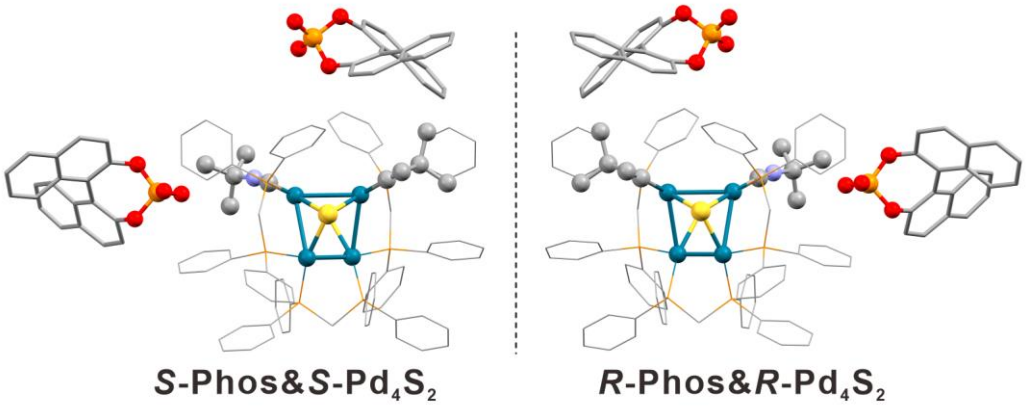

Fig. S18 Enantiomer pair of ***S*-Phos&*S*-Pd$_4$S$_2$** and ***R*-Phos&*R*-Pd$_4$S$_2$**. Color legend: deep sky-blue, Pd; yellow, S; Orange, P; light purple, N; red, O; grey sphere, C. All hydrogen atoms and solvents are omitted for clarity.

Table S1. Crystal data and structure refinement for **Pd_4S_2-*P*4_12_12-twin**.

Identification code	**Pd_4S_2-*P*4_12_12-twin**
Empirical formula	$C_{93}H_{98}N_2O_8P_6Pd_4S_2$
Formula weight	2047.27
Temperature/K	99.99(10)
Crystal system	tetragonal
Space group	*P*4_12_12
a/Å	17.10100(10)
b/Å	17.10100(10)
c/Å	33.2613(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9727.07(13)
Z	4
ρ_{calc}g/cm^3	1.398
μ/mm^{-1}	7.617
F(000)	4160.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.812 to 154.27
Index ranges	$-21 \leq h \leq 20$, $-20 \leq k \leq 21$, $-27 \leq l \leq 41$
Reflections collected	34464
Independent reflections	9760 [R_{int} = 0.0366, R_{sigma} = 0.0318]
Data/restraints/parameters	9760/72/598
Goodness-of-fit on F^2	1.108
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.1084
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.1104
Largest diff. peak/hole / e Å^{-3}	0.85/-0.82
Flack parameter	0.501(13)

Table S2. Crystal data and structure refinement for **Pd_4S_2-*P*4_32_12-twin**.

Identification code	**Pd_4S_2-*P*4_32_12-twin**
Empirical formula	$C_{93}H_{98}N_2O_8P_6Pd_4S_2$
Formula weight	2047.27
Temperature/K	100.00(10)
Crystal system	tetragonal
Space group	*P*4_32_12
a/Å	17.04730(10)
b/Å	17.04730(10)
c/Å	33.2526(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9663.55(13)
Z	4
ρ_{calc}g/cm^3	1.407
μ/mm^{-1}	7.667
F(000)	4160.0
Crystal size/mm^3	0.3 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.826 to 153.362
Index ranges	$-19 \leq h \leq 21$, $-21 \leq k \leq 20$, $-40 \leq l \leq 15$
Reflections collected	33652
Independent reflections	9529 [R_{int} = 0.0434, R_{sigma} = 0.0389]
Data/restraints/parameters	9529/99/597
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0372, wR_2 = 0.0997
Final R indexes [all data]	R_1 = 0.0399, wR_2 = 0.1020
Largest diff. peak/hole / e Å^{-3}	1.38/-0.81
Flack parameter	0.498(11)

Table S3. Crystal data and structure refinement for **Pd_4S_2-*P*4_12_12**.

Identification code	**Pd_4S_2-*P*4_12_12**
Empirical formula	$C_{93}H_{98}N_2O_8P_6Pd_4S_2$
Formula weight	2047.27
Temperature/K	100.00(10)
Crystal system	tetragonal
Space group	*P*4_12_12
a/Å	17.04700(10)
b/Å	17.04700(10)
c/Å	33.2441(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9660.74(14)
Z	4
ρ_{calc}g/cm^3	1.408
μ/mm^{-1}	7.669
F(000)	4160.0
Crystal size/mm^3	0.01 × 0.01 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.826 to 153.934
Index ranges	$-21 \leq h \leq 19$, $-21 \leq k \leq 18$, $-25 \leq l \leq 41$
Reflections collected	28900
Independent reflections	9564 [R_{int} = 0.0347, R_{sigma} = 0.0364]
Data/restraints/parameters	9564/96/574
Goodness-of-fit on F^2	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.1129
Final R indexes [all data]	R_1 = 0.0487, wR_2 = 0.1153
Largest diff. peak/hole / e Å^{-3}	0.95/-0.72
Flack parameter	0.001(4)

Table S4. Crystal data and structure refinement for **Pd_4S_2-*P*4_32_12**.

Identification code	**Pd_4S_2-*P*4_32_12**
Empirical formula	$C_{93}H_{98}N_2O_8P_6Pd_4S_2$
Formula weight	2047.27
Temperature/K	100.00(10)
Crystal system	tetragonal
Space group	*P*4_32_12
a/Å	17.05960(10)
b/Å	17.05960(10)
c/Å	33.1893(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9659.08(14)
Z	4
ρ_{calc}g/cm^3	1.408
μ/mm^{-1}	7.670
F(000)	4160.0
Crystal size/mm^3	0.03 × 0.01 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.824 to 154.59
Index ranges	$-21 \leq h \leq 21$, $-16 \leq k \leq 21$, $-41 \leq l \leq 15$
Reflections collected	31604
Independent reflections	9714 [R_{int} = 0.0368, R_{sigma} = 0.0357]
Data/restraints/parameters	9714/60/599
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0492, wR_2 = 0.1263
Final R indexes [all data]	R_1 = 0.0536, wR_2 = 0.1292
Largest diff. peak/hole / e Å^{-3}	1.47/-0.97
Flack parameter	0.005 (4)

Table S5. Crystal data and structure refinement for **Pd_4S_2-*P*2_1/*n***.

Identification code	**Pd_4S_2-*P*2_1/*n***
Empirical formula	$C_{89}H_{89}N_2O_4P_6Pd_4S_2$
Formula weight	2001.10
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	*P*2_1/*n*
a/Å	19.66120(10)
b/Å	17.71950(10)
c/Å	26.4989(2)
α/°	90
β/°	91.3760(10)
γ/°	90
Volume/Å^3	9229.20(10)
Z	4
ρ_{calc}g/cm^3	1.440
μ/mm^{-1}	8.243
F(000)	4041.0
Crystal size/mm^3	0.3 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.674 to 153.82
Index ranges	$-24 \leq h \leq 24$, $-21 \leq k \leq 19$, $-33 \leq l \leq 32$
Reflections collected	72637
Independent reflections	18705 [R_{int} = 0.0355, R_{sigma} = 0.0293]
Data/restraints/parameters	18705/0/971
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.1138
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.1177
Largest diff. peak/hole / e Å^{-3}	1.61/-1.42

Table S6. Crystal data and structure refinement for **Pd_4S_2-*P*2_1/*n*-MeOH**.

Identification code	**Pd_4S_2-*P*2_1/*n*-MeOH**
Empirical formula	$C_{89}H_{95}N_2O_4P_6Pd_4S_2$
Formula weight	1932.20
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	*P*2_1/*n*
a/Å	19.74432(10)
b/Å	17.37353(9)
c/Å	26.48695(12)
α/°	90
β/°	91.0872(4)
γ/°	90
Volume/Å^3	9084.14(8)
Z	4
ρ_{calc}g/cm^3	1.413
μ/mm^{-1}	8.086
F(000)	3924.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.778 to 153.778
Index ranges	$-23 \leq h \leq 24$, $-21 \leq k \leq 16$, $-33 \leq l \leq 32$
Reflections collected	75730
Independent reflections	18297 [R_{int} = 0.0349, R_{sigma} = 0.0256]
Data/restraints/parameters	18297/0/975
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0328, wR_2 = 0.0842
Final R indexes [all data]	R_1 = 0.0341, wR_2 = 0.0849
Largest diff. peak/hole / e Å^{-3}	0.64/-1.38

Table S7. Crystal data and structure refinement for **Pd_4S_2-*P*2_1/*n*-PF_6^-**.

Identification code	**Pd_4S_2-*P*2_1/*n*-PF_6^-**
Empirical formula	$C_{89}H_{94}F_{12}N_2OP_8Pd_4S_2$
Formula weight	2173.14
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	*P*2_1/*n*
a/Å	19.8370(2)
b/Å	17.6551(2)
c/Å	27.0748(3)
α/°	90
β/°	90.3570(10)
γ/°	90
Volume/Å^3	9482.06(18)
Z	4
ρ_{calc}g/cm^3	1.522
μ/mm^{-1}	8.288
F(000)	4376.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.506 to 153.898
Index ranges	$-24 \leq h \leq 24$, $-22 \leq k \leq 15$, $-28 \leq l \leq 33$
Reflections collected	74727
Independent reflections	19111 [R_{int} = 0.0600, R_{sigma} = 0.0501]
Data/restraints/parameters	19111/0/1071
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0526, wR_2 = 0.1343
Final R indexes [all data]	R_1 = 0.0654, wR_2 = 0.1433
Largest diff. peak/hole / e Å^{-3}	1.95/-1.12

Table S8. Crystal data and structure refinement for ***S*-Phos&*S*-Pd_4S_2**.

Identification code	***S*-Phos&*S*-Pd_4S_2**
Empirical formula	$C_{131}H_{134}N_2O_{15}P_8Pd_4S_2$
Formula weight	2713.87
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	17.89913(7)
b/Å	17.52003(7)
c/Å	20.32819(7)
α/°	90
β/°	107.7876(4)
γ/°	90
Volume/Å^3	6070.04(4)
Z	2
ρ_{calc}g/cm^3	1.485
μ/mm^{-1}	6.542
F(000)	2780.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.806 to 147.572
Index ranges	$-20 \le h \le 22$, $-20 \le k \le 21$, $-25 \le l \le 25$
Reflections collected	113847
Independent reflections	23470 [R_{int} = 0.0336, R_{sigma} = 0.0269]
Data/restraints/parameters	23470/41/1480
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0297, wR_2 = 0.0771
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0784
Largest diff. peak/hole / e Å^{-3}	0.99/-1.10
Flack parameter	-0.017(2)

Table S9. Crystal data and structure refinement for ***R*-Phos&*R*-Pd_4S_2**.

Identification code	***R*-Phos&*R*-Pd_4S_2**
Empirical formula	$C_{131}H_{134}N_2O_{15}P_8Pd_4S_2$
Formula weight	2713.87
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	17.87810(10)
b/Å	17.51700(10)
c/Å	20.33390(10)
α/°	90
β/°	107.6150(10)
γ/°	90
Volume/Å^3	6069.39(7)
Z	2
ρ_{calc}g/cm^3	1.485
μ/mm^{-1}	6.543
F(000)	2780.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.802 to 147.582
Index ranges	$-22 \leq h \leq 22$, $-20 \leq k \leq 21$, $-25 \leq l \leq 23$
Reflections collected	112583
Independent reflections	23507 [R_{int} = 0.0336, R_{sigma} = 0.0249]
Data/restraints/parameters	23507/2876/1477
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0300, wR_2 = 0.0765
Final R indexes [all data]	R_1 = 0.0315, wR_2 = 0.0782
Largest diff. peak/hole / e Å^{-3}	1.07/-1.07
Flack parameter	-0.016(2)

Table S10. The Flack parameters and R_{int} values of 20 spontaneous resolution **Pd_4S_2** crystals grown in the one pot.

Sample number	Space group	Flack parameters	R_{int} values
1	$P4_32_12$	-0.008(5)	4.08%
2	$P4_32_12$	0.001(5)	4.28%
3	$P4_12_12$	0.007(5)	4.19%
4	$P4_12_12$	-0.008(5)	4.42%
5	$P4_32_12$	0.014(7)	5.30%
6	$P4_32_12$	0.007(4)	4.02%
7	$P4_12_12$	-0.004(6)	4.45%
8	$P4_32_12$	0.007(6)	6.04%
9	$P4_32_12$	0.000(9)	5.50%
10	$P4_12_12$	-0.004(5)	4.64%
11	$P4_32_12$	-0.015(5)	4.01%
12	$P4_32_12$	0.017(5)	4.31%
13	$P4_12_12$	0.005(6)	4.07%
14	$P4_32_12$	-0.004(4)	4.13%
15	$P4_12_12$	0.018(5)	4.14%
16	$P4_32_12$	0.012(14)	5.76%
17	$P4_12_12$	0.008(6)	4.01%
18	$P4_12_12$	-0.006(7)	4.35%
19	$P4_32_12$	-0.007(5)	4.00%
20	$P4_12_12$	0.004(5)	4.02%

Table S11. The average volume of individual **Pd_4S_2** clusters with different space groups.

Crystal	Unit cell volume	Z	Unit cell volume/Z
Pd_4S_2-*P*4_12_12-twin	9727.07	4	2431.77
Pd_4S_2-*P*4_32_12-twin	9663.55	4	2415.89
Pd_4S_2-*P*4_12_12	9660.74	4	2415.19
Pd_4S_2-*P*4_32_12	9659.08	4	2414.77
Pd_4S_2- *P*2_1/*n*	9229.20	4	2307.30
Pd_4S_2- *P*2_1/*n*-MeOH	9084.14	4	2271.04
Pd_4S_2- *P*2_1/*n*-PF_6^-	9482.06	4	2370.52

Table S12. Summary of hydrogen bonds, π…π, or C-H…π interactions in **Pd_4S_2-*P*4_12_12**.

Hydrogen bonds	D…A (Å)	H…A (Å)	Symmetry operation
O4-O00U	2.61(2)	1.80	x,y,z
O6-O9	2.48(3)	1.64	x,y,z
C007-O8	3.116(18)	2.15	x,y,z
C009-O9	3.380(16)	2.43	1/2-y,-1/2+x,1/4+z
C105-O8	3.38(4)	2.51	x,y,z
C00I-O8	3.48(2)	2.55	x,y,z
C00K-O00U	3.426(16)	2.51	-1/2+y,1/2-x,-1/4+z
C00N-O4	3.435(19)	2.49	1/2+x,1/2-y,3/4-z
C00O-O3	3.24(2)	2.43	-1/2+y,1/2-x,-1/4+z
C00Q-O1	3.240(17)	2.49	1-y,1-x,1/2-z
C00Y-O6	3.33(2)	2.39	1-y,1-x,1/2-z
C013-O1	3.102(17)	2.35	x,y,z
C01M-O1	3.29(2)	2.42	-1/2+x,3/2-y,3/4-z
π…π	Distance (Å)		Symmetry operation
Cg19-Cg21	3.845(4)		x,y,z
C-H…π	Distance (Å)		Symmetry operation
C015-H015…Cg20	2.92		-1/2+x,1/2-y,3/4-z
C00Z-H00Z…Cg19	2.74		x,y,z

Cg19: phenyl group of C00D, C00F, C00O, C00K, C00P, C00S.
Cg20: phenyl group of C00L, C00X, C013, C00Y, C00T, C010.
Cg21: phenyl group of C00V, C012, C015, C00R, C014, C00J.
The distance of π…π refers to the distance between the centroids of the phenyl groups.
The distance of C-H…π refers to the distance between the H atom and the centroid of the phenyl group.

Table S13. Number of HOAc, OAc^-, and MeOH in different **Pd_4S_2** crystals as determined by ^1H NMR.

Crystals	HOAc	OAc^-	MeOH
Pd_4S_2-*P*4_12_12/*P*4_32_12	3	2	0
Pd_4S_2-*P*4_12_12/*P*4_32_12-twin	3	2	0
Pd_4S_2-*P*2_1/*n*	≈1	2	0
Pd_4S_2-*P*2_1/*n*-MeOH	0	2	≈2

Table S14. Crystal data and structure refinement for ***S*-Phos&*R*-Pd_4S_2**.

Identification code	***S*-Phos&*R*-Pd_4S_2**
Empirical formula	$C_{125}H_{108}N_2O_8P_8Pd_4S_2$
Formula weight	2503.61
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	19.34060(10)
b/Å	17.25180(10)
c/Å	37.5232(4)
α/°	90
β/°	96.3380(10)
γ/°	90
Volume/$Å^3$	12443.47(14)
Z	4
$\rho_{calc}g/cm^3$	1.336
μ/mm^{-1}	6.296
F(000)	5088.0
Crystal size/mm^3	0.05 × 0.02 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.596 to 130.178
Index ranges	$-22 \leq h \leq 22$, $-20 \leq k \leq 20$, $-44 \leq l \leq 44$
Reflections collected	216526
Independent reflections	42048 [R_{int} = 0.0712, R_{sigma} = 0.0507]
Data/restraints/parameters	42048/3115/2215
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0851, wR_2 = 0.2234
Final R indexes [all data]	R_1 = 0.0919, wR_2 = 0.2282
Largest diff. peak/hole / e $Å^{-3}$	2.63/-1.47
Flack parameter	0.058(12)

Table S15. Crystal data and structure refinement for ***R*-Phos&*S*-Pd_4S_2**.

Identification code	***R*-Phos&*S*-Pd_4S_2**
Empirical formula	$C_{125}H_{108}N_2O_8P_8Pd_4S_2$
Formula weight	2503.61
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	19.37370(10)
b/Å	17.25020(10)
c/Å	37.8551(3)
α/°	90
β/°	96.7660(10)
γ/°	90
Volume/Å^3	12563.07(14)
Z	4
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	6.236
F(000)	5088.0
Crystal size/mm^3	0.05 × 0.05 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.594 to 155.504
Index ranges	$-24 \leq h \leq 24$, $-21 \leq k \leq 21$, $-47 \leq l \leq 47$
Reflections collected	244642
Independent reflections	50499 [R_{int} = 0.0666, R_{sigma} = 0.0481]
Data/restraints/parameters	50499/1958/2407
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0722, wR_2 = 0.1814
Final R indexes [all data]	R_1 = 0.0773, wR_2 = 0.1848
Largest diff. peak/hole / e Å^{-3}	1.43/-1.47
Flack parameter	0.043(8)

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