Supplementary Information for

Safe P_4 reagent in a reusable porous coordination network

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Experimental Details

Reagents

All the chemicals were used without any further purification. TPT (TPT = 2,4,6-tris(4-pyridyl)-1,3,5-triazine) was synthesized according to the procedure described in the reference S1; single crystalline network **1** and powder crystalline network **1** were prepared according to the procedure described in the reference S2 and S3, respectively.

Methods

Single X-ray diffraction data were measured on a KAPPA APEX2 QUAZAR Mo instrument in house (Mo Kα, λ = 0.71073 Å). Powder X-ray diffraction data were collected on a Bruker D8 ADVANCE instrument in house (Cu $K\alpha_1$, λ = 1.5406 Å). High quality powder X-ray diffraction data for *ab initio* powder structure analysis were collected at SPring-8 (BL15XU), the details are described below. FTIR spectra were recorded on a Varian 670-IR FT-IR spectrometer (650–4000 cm^{-1}). Elemental analyses were performed by Vario MICRO Cube (Elementar) at Technical Support Center in Pohang University of Science and Technology. Thermogravimetry (TG) / differential scanning calorimetry analysis (DSC) were carried out at a ramp rate of 20 K/min in a nitrogen flow (50 ml/min) with a Setaram Labsys Evo instrument. ^{31}P NMR were measured by Bruker Advance III (FT-NMR 500MHz).

Preparation of single crystalline P_4@network 1

Single crystals of network **1** (40.0 mg, 0.025 mmol) and red phosphorus (20 mg, 0.645 mmol) were separately placed into a glass tube (ca. 30 cm, 17 mL) as shown in Figure S1. The tube was sealed under *ca.* 0.37 Torr after the network **1** was activated at 500 K for 20 min. Whole part of the glassware was put in an oven and heated at 673 K for 10 h. After heating, the glassware was cooled rapidly at 300 K for 10 minutes. The glassware was opened in air without special care, and the pale green solids (32 mg, yield 80 %) were collected.

Elemental Analysis

Found : C, 26.13; H, 1.511; N, 10.102.

Calc. for $C_{36}H_{25.48}I_6N_6O_{0.74}P_{1.08}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.27}(H_2O)_{0.74}]\}$: C, 26.76; H, 1.50; N, 10.40.

Preparation of powder crystalline P_4@network 1

Powder crystalline network **1** (150.0 mg, 0.0948 mmol) and red phosphorus (28.0 mg, 0.421 mmol) were separately placed into a glass tube (ca. 30 cm, 17 mL). The tube was sealed under ca. 0.37 Torr after the network **1** was activated at 500 K for 20 min. Whole part of the glassware was put in an oven and heated at 673 K for 10 h. After heating, the glassware was cooled rapidly at 300 K for 10 minutes. The glassware was opened in air without special care, and the pale green solids (120 mg, yield 80 %) were collected.

Elemental Analysis

Found : C, 25.53; H, 1.56; N, 9.93.

Calc. for $C_{36}H_{24.12}I_6N_{12}O_{0.06}P_{3.76}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.94}(H_2O)_{0.06}]\}$: C, 25.44; H, 1.43; N, 9.89.

Air stability of powder crystalline P_4@network 1

On one side, about 50 mg of P_4@network **1** (powder) was well spread out on the paper and covered by transparent glass to protect from dust; on the other side, the same amount of P_4@network **1** (powder) was put on the paper and covered by glass wrapped by aluminium foil to protect from visible light (Fig. S10). Both P_4@network **1** covered by transparent glass and aluminium foil were exposed by visible light for 6 days in ambient condition. After 6 days, although colour of the P_4@network **1** covered by transparent glass changed from pale green to pale red, colour of the P_4@network **1** covered by aluminium foil did not change. Even after 3 months, the colour of the network covered by foil did not change. The XRPD patterns of the network after visible light exposure were changed only for the sample covered by transparent glass as shown in Figure S12.

Extraction of P_4 from powder crystalline P_4@network 1 by immersing in nitrobenzene

First, P_4@network **1** (powder) (16.98 mg, 10.0 μmol) was put into bottom of an Young NMR tube. Second, Triphenylphosphine (0.263 mg, 1.0 μmol) was dissolved in the mixture solution of nitrobenzene (0.5 mL) and d_5-nitrobenzene (0.2 mL), and the solution was filled into the tube. The tube was filled by high purity (99.999 %) Ar. ^{31}P NMR (500 MHz, Triphenylphosphine) was measured continuously every 1.5 min. at 300 K for 1 day. From the beginning of the measurement, one peak appeared at -523.1 ppm, and intensity of peak increased as time goes by.

For extraction in elevated temperature, 423 K, the same amount of P_4@network **1**, nitrobenzene, and d_5-nitrobenzene were put into two 8 mL vial, respectively, and Ar was continuously introduced. Each bottom of vial was heated at 423 K for 5 and 15 minutes, respectively. After heating, resultant solution and 0.263 mg of triphenylphosphine were mixed well, and ^{31}P NMR were measured. The results of ^{31}P NMR are shown in table S4.

P_4 extraction by heating in glass under reduced pressure

In pyrex tube (ca. 30 cm, 17 mL), a glassware filled by 100.0 mg (0.05916 mol) of P_4@network **1** (powder) was inserted gently. The tube was sealed under 0.34 Torr, and network part was immersed into oil bath. Above 410 K, colourless, waxy material was formed onto the opposite part of glass tube. Waxy material was collected at 500 K for 1 h. After collecting, glass was cut inside of glove bag filled with N_2. The waxy material was washed with d_6-DMSO; 0.6 mL of solution was put into an NMR tube with 5.0 μL of H_3PO_4, and then ^{31}P NMR was measured.

P_4 regeneration by heating under vacuum

In pyrex tube (ca. 30 cm, 17 mL), a glassware filled by 340.0 mg (0.2002 mmol) of P_4@network **1** (powder) was inserted gently. Glass was connected to vacuum line through cold trap. The pressure of inside the glass was reduced to 0.1 Torr; the whole part of network was immersed into oil bath and heated at 500 K for 6 h (activation). After heating, the colour of the network recovered to pale yellow, indicating the original network **1** was recovered. The weight loss of network was carefully measured and result suggested 3.58 % decreasing, which is corresponding to 52.8 % of P_4 in the pore of network.

The activated network **1** was reused for P_4 trapping in the same manner with first trapping condition.

The recovered network and reused network were measured by XRPD (Fig. 3).

Single crystal X-ray structure determination

The diffraction data for P_4@network **1** (single) was recorded with a Bruker CCD X-ray diffractometer with a Mo target (λ = 0.71073 Å) in laboratory. The diffraction images were processed by using APEX 2.

For the structure of P_4@network **1** at 300 K, the structure was solved by direct methods (SHELXS-2014) and refined by full-matrix least squares calculations on F^2 (SHELXL-2014) using the SHELX-TL program package.

For the structure of P_4@network **1** at 100 K, non-merohedral twin was found. The orientation matrices for the two components were identified using the program CELL_NOW, with two components being related by a 180 degree rotation around *a*- (*a**-) axis. The two components were integrated using SAINT, resulting in the following statistics:

Statistics for singles of twin component 1

Scan	2-theta	R(int)	Incid. factors	Diffr. Factors	K	Total	I>2sig(I)
1	-13.7	0.0980	0.701 - 1.235	0.908 - 1.091	0.628	4974	3067
2	13.6	0.0955	0.854 - 1.129	0.900 - 1.167	0.616	8128	4991
3	-13.7	0.0822	0.584 - 0.788	0.925 - 1.167	0.619	4707	3178
4	-13.7	0.0724	0.540 - 0.603	0.870 - 1.112	0.617	4043	2926
5	-13.7	0.0755	0.559 - 0.679	0.872 - 1.151	0.665	4834	3178
6	13.7	0.0999	0.631 - 1.468	0.898 - 1.167	0.635	7123	4255
7	-13.7	0.0765	0.505 - 0.723	0.889 - 1.136	0.639	4814	3350
All scans		0.0878	0.505 - 1.468	0.870 - 1.167	0.631	38623	24945

Statistics for singles of twin component 2

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Scan	2-theta	R(int)	Incid. Factors	Diffr. Factors	K	Total	I>2sig(I)
1	-13.7	0.1873	0.572 - 0.947	0.917 - 1.136	0.628	4924	2064
2	13.6	0.1806	0.663 - 0.887	0.921 - 1.208	0.616	8149	3483
3	-13.7	0.1534	0.518 - 0.668	0.938 - 1.208	0.619	4664	2235
4	-13.7	0.1373	0.465 - 0.516	0.874 - 1.155	0.617	4076	2098
5	-13.7	0.1382	0.468 - 0.575	0.879 - 1.185	0.665	4827	2325
6	13.7	0.1846	0.556 - 1.085	0.913 - 1.208	0.635	7063	2953
7	-13.7	0.1509	0.459 - 0.658	0.896 - 1.154	0.639	4819	2370
All scans		0.1655	0.459 - 1.085	0.874 - 1.208	0.631	38522	17528

The exact twin matrix identified by the integration program was found to be

(1.00005 -0.00057 0.07137/ -0.01300 -0.99999 0.00531/-0.00154 -0.00104 -1.00005).

The data were corrected for absorption using TWINABS, and the structure was solved using direct methods with all components. The structure was refined using the hkl 5 routine with all reflections of component 1, resulting BASF value of 0.22058.

The Rint value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2012))

For the structure of P_4@network **1** at 200 K, also non-merohedral twin was found. The orientation matrices for the two components were identified using the program CELL_NOW, with two components being related by a 180 degree rotation around *a*- (*a**-) axis. The two components were integrated using SAINT, resulting in the following statistics:

```
 Statistics for singles of twin component    1
   ------------------------------------------
 Scan   2-theta  R(int)   Incid. Factors   Diffr. Factors   K       Total  I>2sig(I)
   1    -12.9    0.0821   0.645 - 0.994    0.915 - 1.093    0.600   7127    4186
   2    12.9     0.0816   0.671 - 0.794    0.883 - 1.129    0.610   4492    2709
   3    12.9     0.0755   0.656 - 0.734    0.885 - 1.108    0.605   5430    3517
   4    -12.9    0.0737   0.653 - 0.781    0.883 - 1.128    0.635   4892    2937
   5    12.9     0.0792   0.679 - 0.807    0.882 - 1.025    0.624   4765    2847
   6    12.8     0.0820   0.783 - 0.950    0.950 - 1.129    0.596   8223    4836
   7    -12.9    0.0870   0.900 - 1.011    0.953 - 1.129    0.618   5730    3292
 All scans    0.0804      0.645 - 1.011    0.882 - 1.129    0.613   40659   24324

   Statistics for singles of twin component    2
   ------------------------------------------
 Scan   2-theta  R(int)   Incid. Factors   Diffr. Factors   K       Total  I>2sig(I)
   1    -12.9    0.1812   0.570 - 0.876    0.925 - 1.160    0.600   7120    2725
   2    12.9     0.1802   0.583 - 0.696    0.886 - 1.179    0.610   4472    1784
   3    12.9     0.1552   0.561 - 0.663    0.886 - 1.118    0.605   5468    2238
   4    -12.9    0.1582   0.558 - 0.725    0.885 - 1.177    0.635   4912    1886
   5    12.9     0.1667   0.571 - 0.758    0.885 - 1.088    0.624   4754    1822
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6	12.8	0.1789	0.637 - 0.802	0.945 - 1.180	0.596	8210	3158
7	-12.9	0.1850	0.663 - 0.857	0.939 - 1.180	0.618	5660	2131
All scans		0.1731	0.558 - 0.876	0.885 - 1.180	0.613	40596	15744

The exact twin matrix identified by the integration program was found to be
(1.00007 -0.00048 0.06580/-0.01099 -0.99999 0.00547/-0.00210 -0.00104 -1.00007).

The data were corrected for absorption using TWINABS, and the structure was solved using direct methods with all components. The structure was refined using the hkl 5 routine with all reflections of component 1, resulting BASF value of 0.18655.

The Rint value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2012)).

X-ray Crystallographic data for P_4@network 1 single crystal at 100 K

$C_{36}H_{24}I_6N_{12}P_{1.08}Zn_3$ M_r = 1615.7, crystal dimensions 0.09 × 0.05 × 0.04 mm^3, monoclinic, space group $P2_1/m$, a = 6.5194(6), b = 30.015(3) Å, c = 12.7207(11) Å, β = 94.015(4)°, V = 2483.0(4) $Å^3$, Z = 2, ρ_{calcd} = 2.158 g cm^{-3}, μ = 5.238 mm^{-1}, λ = 0.71073 Å (Mo $K\alpha$), T = 100(2) K, 4156 unique reflections out of 5189 with $F_0 > 4\sigma(F_0)$, 285 parameters, 1 restraints, $1.357 < \theta < 26.446$ °, final R factors $R1$ = 0.0481 and $wR2$ =0.0932, GOF = 1.074. CCDC deposit number:1440074.

X-ray Crystallographic data for P_4@network 1 single crystal at 200 K

$C_{36}H_{24}I_6N_{12}P_{1.08}Zn_3$ M_r = 1615.7, crystal dimensions 0.09 × 0.05 × 0.04 mm^3, monoclinic, space group $P2_1/m$, a = 6.5441(4), b = 30.1738(18) Å, c = 12.7487(8) Å, β = 93.705(3)°, V = 2512.1(3) $Å^3$, Z = 2, ρ_{calcd} = 2.133 g cm^{-3}, μ = 5.178 mm^{-1}, λ = 0.71073 Å (Mo $K\alpha$), T = 200(2) K, 3593 unique reflections out of 4862 with $F_0 > 4\sigma(F_0)$, 285 parameters, 1 restraints, $1.350 < \theta < 25.727$ °, final R factors $R1$ = 0.0464 and $wR2$ =0.0865, GOF = 1.033. CCDC deposit number:1440075.

X-ray Crystallographic data for P_4@network 1 single crystal at 300 K

$C_{36}H_{24}I_6N_{12}P_{1.08}Zn_3$ M_r = 1615.7, crystal dimensions 0.09 × 0.05 × 0.04 mm^3, orthorhombic, space group $P2_1/m$, a = 6.6025(6), b = 30.199(3) Å, c = 12.8199(12) Å, V = 2556.1(4) $Å^3$, Z = 2, ρ_{calcd} = 2.092 g cm^{-3}, μ = 5.078 mm^{-1}, λ = 0.71073 Å (Mo $K\alpha$), T = 300(2) K, 1596 unique reflections out of 2373 with $F_0 > 4\sigma(F_0)$, 285 parameters, 18 restraints, $1.349 < \theta < 23.313$ °, final R factors $R1$ = 0.0554 and $wR2$ =0.0987, GOF = 1.041. CCDC deposit number: 1457373.

Ab initio XPRD analysis

Ab Initio crystal structure determination of $[(ZnI_2)_3(TPT)_2(P_4)_{0.94}]$ (P_4@network 1).

High quality powder X-ray diffraction pattern of P_4@network **1** was recorded at 134 K in transmission mode [0.3 mm capillary; synchrotron radiation λ = 0.652970 Å; 2θ range, 0.00294 to 35.8726°; step width, 0.003°; data collection time, 100 sec] on a diffractometer equipped with a white imaging plate detector at BL15XU NIMS beam line, SPring-8.

The XRPD pattern of P_4@network **1** was indexed using the program DICVOL (Boultif, A.; Louër, D. *J. Appl. Crystallogr*. **1991**, *24*, 987-993) to give a monoclinic unit cell (a = 12.70811 Å, b = 30.55229 Å, c = 6.51127 Å, β = 95.489°, V = 2516.485 Å^3) with good figure of merit. The space group was assigned from systematic absences as $P2_1$ or $P2_1/m$. We determined it as $P2_1$/m from the result of single crystal data. Unit cell and profile refinement were carried out using the Pawley method, led to good fit (χ^2 = 31.810) for these lattice parameters and space group. Structure solution was carried out by the simulated annealing method with the program DASH (David, W. I. F.; Shankland, K; van de Streek, J; Pidcock, E; Motherwell, W. D. S.; Cole, J. C, *J. Appl. Crystallogr.,* **2006**, *39*, 910-915). Two rigid groups; $[(ZnI_2)_3(TPT)_2]_{0.5}$ in which Zn-$N_{pyridyl}$ were allowed to rotate and P_4 molecule, in asymmetric unit and Z = 2 for space group $P2_1$/m were introduced by using a constrained Z-matrix description. During annealing, 25 runs of 1×10^7 Monte Carlo moves each were performed. The best structure obtained (Profile χ^2 = 178.65) was taken as the starting structural model for Rietveld refinement.

The Rietveld refinement of P_4@network **1** was performed with the program RIETAN-FP (Izumi, F.; Momma, K. *Solid State Phenom*., **2007**, *130*, 15-20) and VESTA (Momma, K.; Izumi, F. *J. Appl. Crystallogr*., **2008**, *41*, 653-658). Restraints but no constraints for all bond lengths were employed to maintain the molecular geometry. Atomic displacement parameters were refined isotropically with uniform values. We did not fix the iodine atoms at special position because if we fix the iodine, the refinement results show higher residuals (R_{wp} = 7.9%). Therefore, iodine was split (disordered) to two positions by mirror plane.

Final Rietveld refinement result for $P2_1/\mathrm{m}$ space group: a = 12.7069(3) Å, b = 30.5552(8) Å, c = 6.5079(2) Å, β = 95.488(2)°,V = 2515.2(1) Å^3, R_{wp} = 5.067% (R_{e} = 31.218%), R_{p} = 4.340%, R_{B} = 4.738%, R_{F} = 1.782%; 10534 profile points (2θ range, 2.5026 to 33.9962°); 270 refined variables. The result is shown in Figure S5b. CCDC deposit number : 1440077.

Quantum Chemical Calculation

The interaction between P_4 and Iodide was examined by single point calculation (MP2/LanL2DZ) of the $[ZnI_2(py)_2]\ldots P_4$ (py = 4-pyridine) in which the geometry was extracted from the structure determined by single crystal X-ray diffraction at 100 K. Because energy for the interaction cannot be well described by this calculation, we paid attention to Mulliken charges. $I\ldots P_4$ Mulliken charge suggests charge transfer, because far lying P atoms are negatively charged as indicated in Figure S3.

Further confirmation of the orbital interaction was performed by calculation of P_4 unit and $[ZnI_2(py)_2]$ unit separately by MP2/6-31G*+ level (Iodine was treated by ECP:LanL2DZ). The HOMO and LUMO of P_4 and $[ZnI_2(py)_2]$ were depicted in Figure S4. Because HOMO of $[ZnI_2(py)_2]$ composed of iodide p-orbitals has higher energy than LUMO of P_4 composed of p-orbitals, the interaction between P_4 unit and $[ZnI_2(py)_2]$ unit should has charge transfer character from I^- to P_4 with overlap of p-orbitals.

Repeating P_4 regeneration by heating at 500 K under reduced pressure

First trapping:

Powder crystalline network **1** (400.0 mg, 0.2528 mmol) and red phosphorus (200.0 mg, 6.457 mmol) were separately placed into a glass tube (ca. 30 cm, 17 mL). The tube was sealed under *ca*. 0.37 Torr after the network **1** was activated at 500 K for 20 min. Whole part of the glassware was put in an oven and heated at 673 K for 10 h. After heating, the glassware was cooled rapidly at 300 K for 10 minutes. After trapping, the colour of the network became pale green.

First activation (extraction):

In pyrex tube (ca. 30 cm, 17 mL), a glassware filled by 257.59 mg (0.1522 mmol) of P_4@network **1** was inserted gently. For activation, the pyrex tube was connected to vacuum line through cold trap, and the inner pressure was reduced to 0.1 Torr; the whole part of network was immersed into oil bath and heated at 500 K for 10 h. After heating, the colour of the network recovered to pale yellow. The weight loss of network was carefully measured and result suggested 5.40 % decreasing, which is corresponding to 83.9 % of P_4 in the pore of network.

Second trapping:

Powder crystalline network **1** (225.0 mg) obtained from first activation and red phosphorus (112.5 mg, 3.631 mmol) were separately placed into a glass tube (ca. 30 cm, 17 mL). Following methods were the same as first trapping as described above. After heating, the colour of the network became dark green.

Second activation (extraction):

In pyrex tube (ca. 30 cm, 17 mL), a glassware filled by 160.92 mg of P_4@network **1** was inserted gently. Following methods were the same as first activation as described above. After heating, the colour was maintained. The weight loss of network was carefully measured and result suggested 4.80 % decreasing, which is corresponding to 73.7 % of P_4 in the pore of network.

Third trapping:

Powder crystalline network **1** (125.0 mg) obtained from second activation and red phosphorus (62.5 mg, 2.018 mmol) were separately placed into a glass tube (ca. 30 cm, 17 mL). Following methods were the same as first activation as described above. After heating, the colour was maintained.

Third activation (extraction):

In pyrex tube (ca. 30 cm, 17 mL), a glassware filled by 94.09 mg of P_4@network **1** was inserted gently. Following methods were the same as first activation as described above. After heating, the colour was maintained. The weight loss of network was carefully measured and result suggested 4.45 % decreasing, which is corresponding to 69.1 % of P_4 in the pore of network.

The results of P_4@network **1** activation and regeneration were summarized in Table S5. The colour change of network was shown in Figure S15; the XRPD change was shown in Figure S16.

Repeating P_4 regeneration by extraction in nitrobenzene at 423 K

First trapping:

Powder crystalline network **1** (200.0 mg, 0.1264 mmol) and red phosphorus (100.0 mg, 3.228 mmol) were separately placed into a glass tube (ca. 30 cm, 17 mL). The tube was sealed under ca. 0.37 Torr after the network **1** was activated at 500 K for 20 min. Whole part of the glassware was put in an oven and heated at 673 K for 10 h. After heating, the glassware was cooled rapidly at 300 K for 10 minutes. After trapping, the colour of the network became pale green.

First extraction and activation:

P_4@network **1** (powder) (160.0 mg, 0.09454 mmol) was put into a bottom of round flask, and 30 mL of nitrobenzene was mixed. The flask was heated at 423 K for 15 h with stirring, and high purity Ar (99.999 %) gas was continuously bubbled through needle. After heating, powder was filtered with fresh nitrobenzene and washed by diethyl ether. The colour of washed powder recovered to pale yellow. The powder washed by ether was used for EA measurement.

To remove nitrobenzene from the pore of the network, the powder was put into pyrex tube, and the tube was heated at 500 K for 3 h in oil bath during pumping out under 0.1 Torr.

Second trapping:

Powder crystalline network **1** (120.0 mg) obtained from first activation and red phosphorus (60.0 mg, 1.937 mmol) were separately placed into a glass tube (ca. 30 cm, 17 mL). Following methods were the same as first trapping as described above. After heating, the glassware was cooled rapidly at 300 K for 10 minutes. After trapping, the colour of the network became pale green.

Second extraction and activation:

P_4@network **1** (powder) (75.0 mg) was put into a bottom of round flask, and 30 mL of nitrobenzene was mixed. Following methods were the same as first activation as described above. The colour of washed powder was maintained. The powder washed by ether was used for EA measurement.

To remove nitrobenzene from the pore of the network, the powder was put into pyrex tube, and the tube was heated at 500 K for 3 h in oil bath during pumping out under 0.1 Torr.

Third trapping:

Powder crystalline network **1** (56.0 mg) obtained from second activation and red phosphorus (26.0 mg, 0.8394 mmol) were separately placed into a glass tube (ca. 30 cm, 17 mL). Following methods were the same as first trapping as described above. After heating, the glassware was cooled rapidly at 300 K for 10 minutes. After trapping, the colour of the network became dark green.

Third extraction and activation:

P_4@network **1** (powder) (32.0 mg) was put into a bottom of round flask, and 30 mL of nitrobenzene was mixed. Following methods were same as first activation as described above. The colour of washed powder was maintained. The powder washed by ether was used for EA measurement.

To remove nitrobenzene from the pore of the network, the powder was put into pyrex tube, and the tube was heated at 500 K for 3 h in oil bath during pumping out under 0.1 Torr.

The results of P_4@network **1** extraction and regeneration were summarized in Table S6. The colour change of network was shown in Figure S15; the XRPD change was shown in Figure S17.

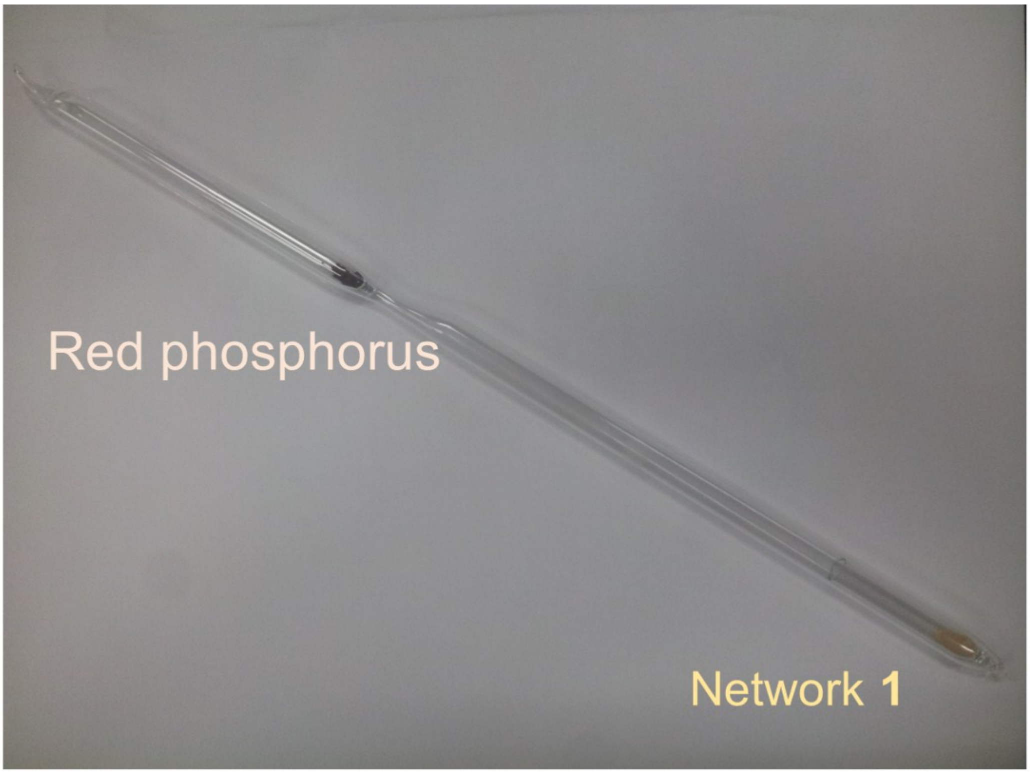

Figure S1. Experimental set-up of glassware for vapour phase diffusion of P_4 from red phosphorus into network **1**.

Table S1. Comparison of geometrical parameters from X-ray analysis

	Single Crystal 100K	Single Crystal 200K	Single Crystal 300K	Powder 134K
Zn-I (top) / Å	2.549(2), 2.523(2)	2.545(2), 2.519(2)	2.539(5), 2.523(5)	2.520(17), 2.476(17)
Zn-I (connector) / Å	2.567(1), 2.529(1)	2.524(1), 2.562(1)	2.519(2), 2.554(2)	2.600(7), 2.549(7)
P-P / Å	2.14(2), 2.16(2), 2.18(2), 2.21(3)	2.11(2), 2.18(3), 2.12(3), 2.17(3)	2.10(11), 2.04(8), 2.01 (5), 2.10(8)	2.23(5), 2.22(4), 2.15(5), 2.19(6)
I…P / Å	3.689(8), 3.689(12)	3.710(11), 3.715(14)	3.71(5), 3.65(4)	3.71(3),
Occ. of P	0.270(1)	0.270(1)	0.270(11)	$0.94^{\#}$

\# Occ. of P_4 for each disordered P_4 is fixed as 0.47.

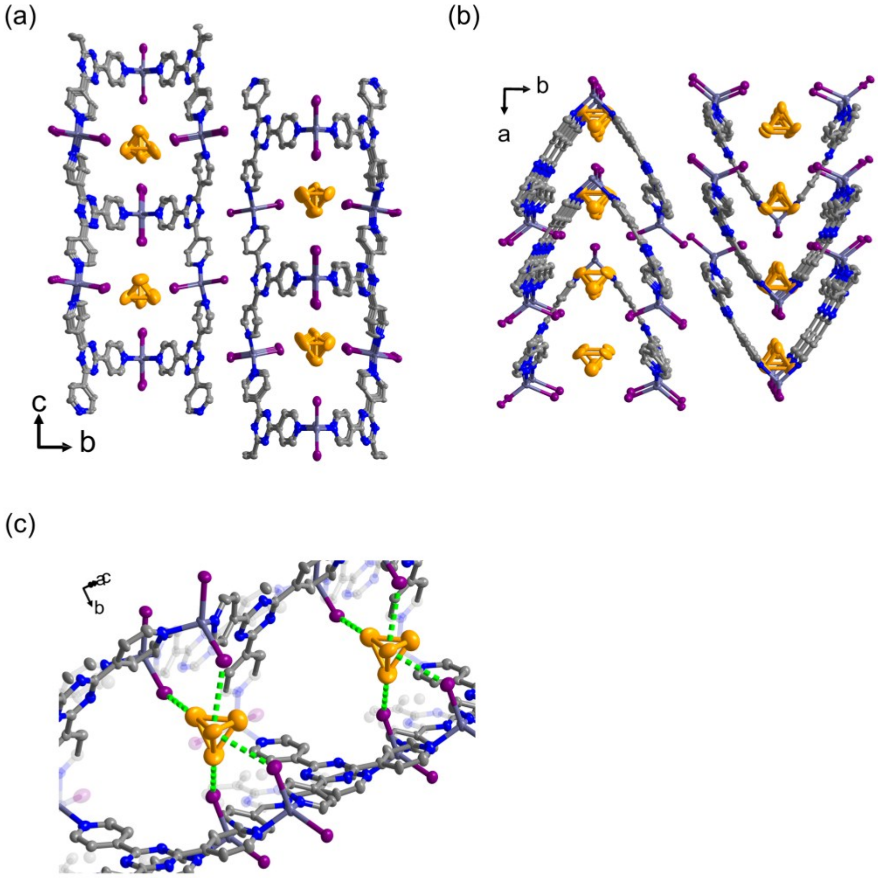

Figure S2. Crystal structures (ORTEP plots, 50% probability) of single crystal P_4@network **1** determined by single crystal analysis at 200 K: (a) view along *a*-axis, (b) view along *c*-axis, (c) interaction description.

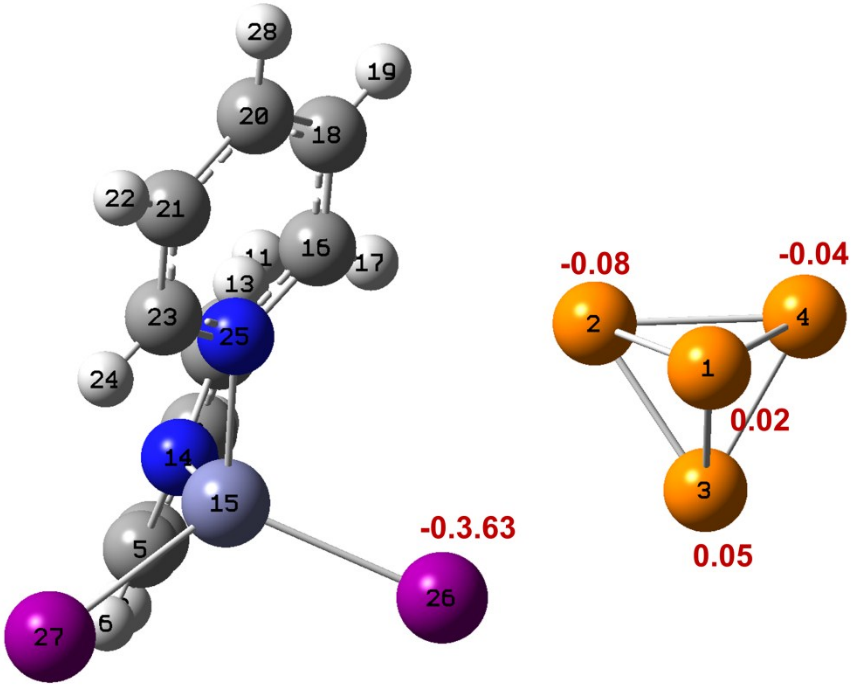

Figure S3. Mulliken charge in $[ZnI_2(py)_2]\ldots P_4$

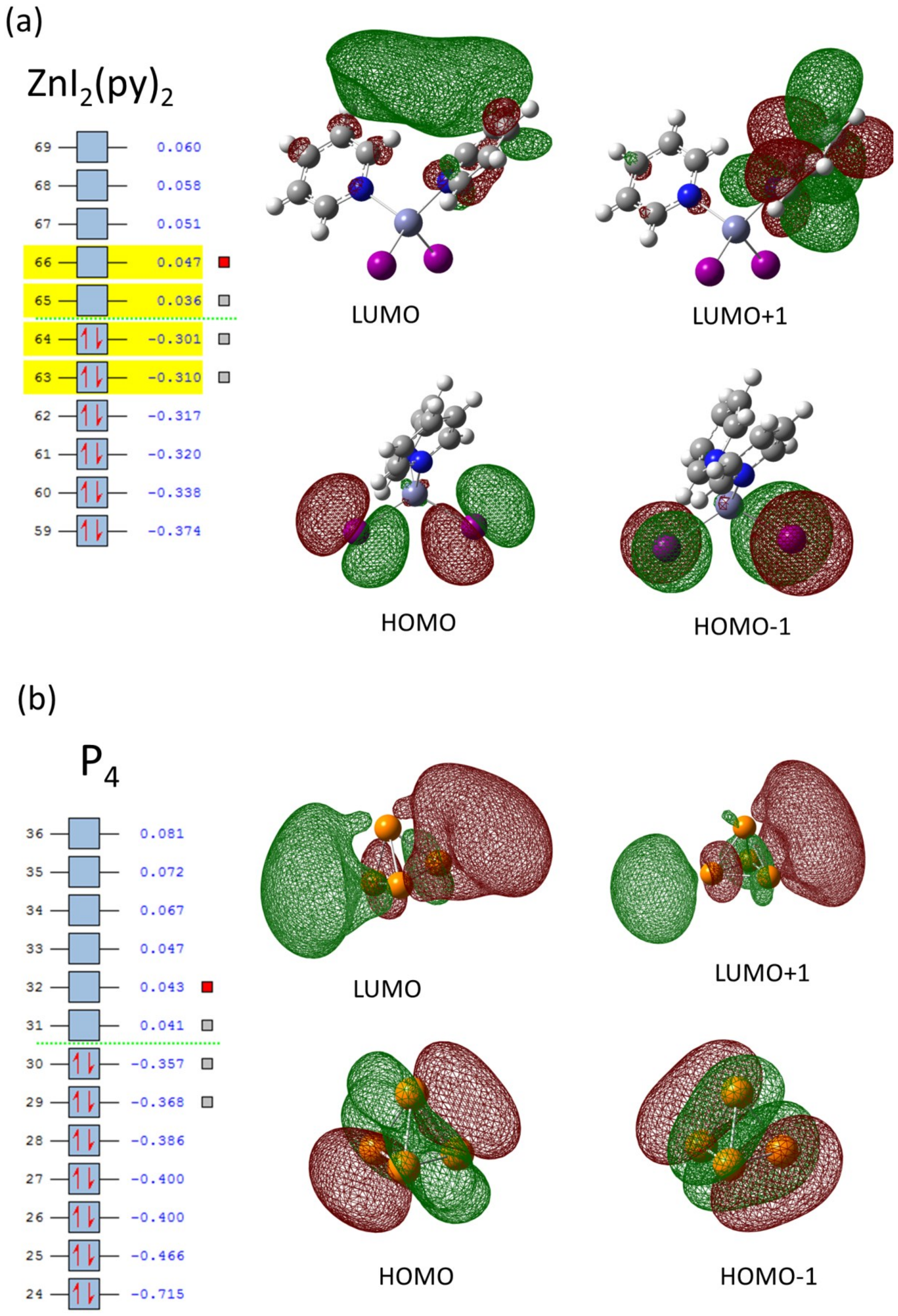

Figure S4. Molecular orbitals of (a) [$ZnI_2(py)_2$] and (b) P_4.

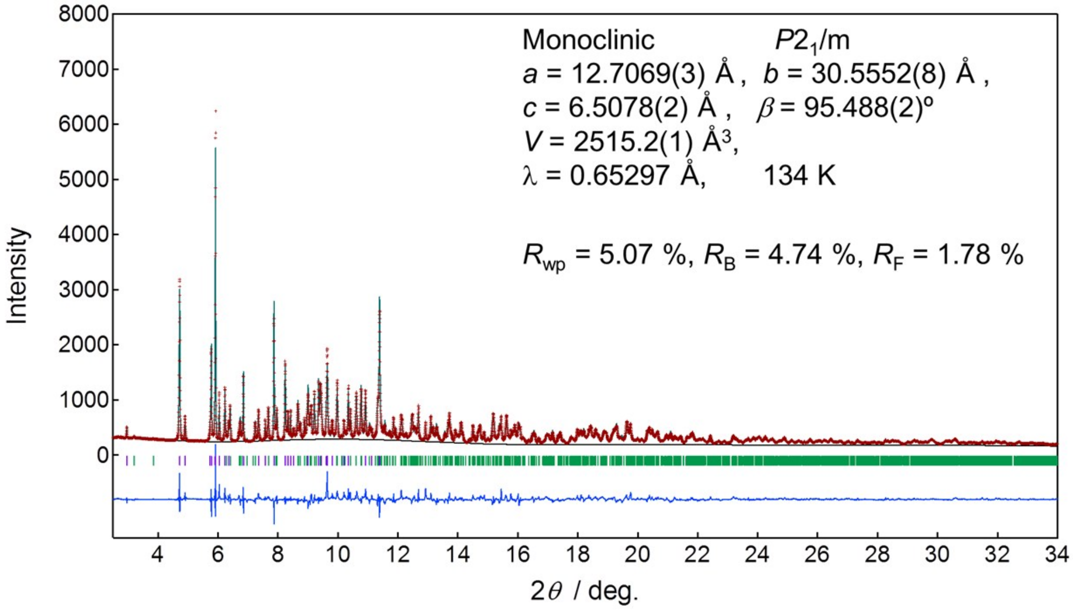

Figure S5. Experimental (red), calculated (black), and difference (blue) XRPD profiles from the final Rietveld refinement of P_4@network **1**

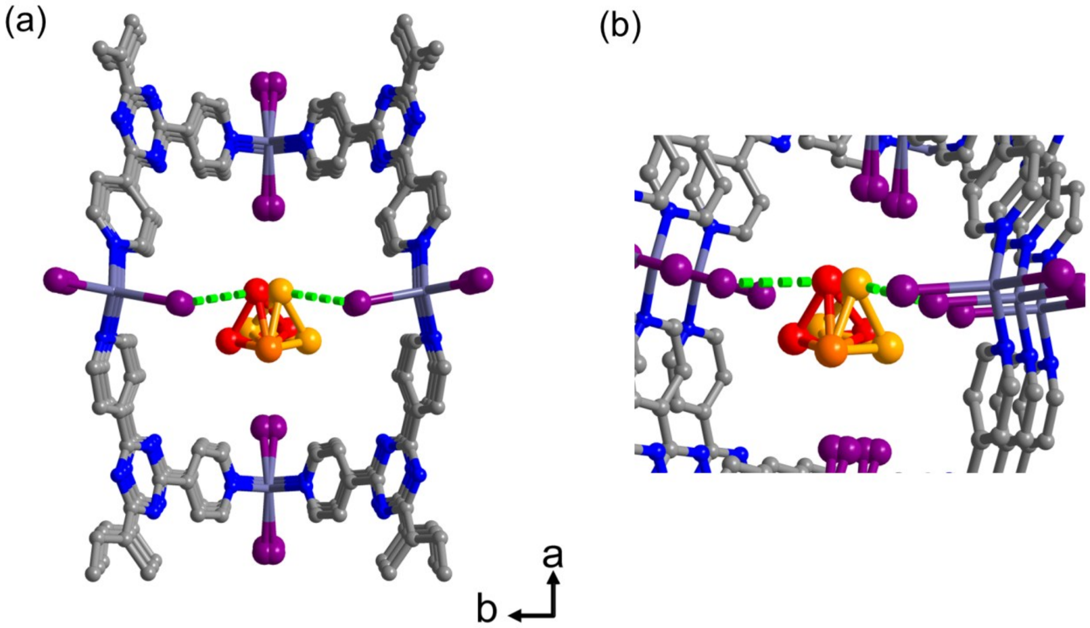

Figure S6 Crystal structures of powder crystalline P_4@network **1** determined by ab initio XRPD analysis (a) view along *c*-axis, (b) description of interaction between P_4 and iodide. Colour codes: C, grey; N, blue; P, orange and red; Zn, pale-blue; and I, purple. Green dotted line shows interactions.

Table S2. Comparison of site occupancy of P_4 in single crystalline P_4@network 1*

Dimension of crystal	**90** x **50** x **40** μm^3	**90** x **40** x **20** μm^3	**90** x **20** x **20** μm^3
SOF	0.257(18)	0.26(2)	0.264(10)

*Each crystal was picked up from the same P_4-trapping reaction.

Table S3. Mass ratio comparison (trapping P_4 / compound) with previous reports

Compound	$\{(P_4)_2C_{60}\}$	$[Cu_2Cl_2\{Cp^*Fe(\eta^5\text{-}P_5)\}_2](P_4)$	$\{[(ZnI_2)_3(C_{18}H_{12}N_6)_2(P_4)_{0.94}(H_2O)_{0.06}]\}$	$4(C_4H_{12}N^+)$, $C_{144}H_{96}Fe_4N_{24}O_{36}S_{12}{}^{4-}$, $0.75(P_4)$, $38.5(H_2O)$
Trapping P_4 / total mass	0.2559[a]	0.1222[b]	0.06851[c]	0.02098[d]
Reference	*J. Chem. Soc., Chem. Commun.* **1994**, 1367-1368	*Angew. Chem. Int. Ed.* 2013, **52**, 10896-10899	This work **	Science, 2009, **324**, 1697-1699

*Cp= η^5-C_5Me_5

**Trapping amount was calculated based on the EA result (in page S4) that used for *ab initio* XRPD analysis.

a. MW of compound $\{(P_4)_2C_{60}\}$ = 968.4, (MW of P_4) x (number of P_4 in compound) = 247.8,

∴ (Trapping P_4 / total mass) = 247.8 / 968.4 = 0.2559

b. MW of compound $[Cu_2Cl_2\{Cp^*Fe(\eta^5\text{-}P_5)\}_2](P_4)$ = 1013.8, (MW of P_4) x (number of P_4 in compound) = 123.9

∴ (Trapping P_4 / total mass) = 123.9 / 1013.8 = 0.1222

c. MW of compound $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.94}(H_2O)_{0.06}]\}$ = 1699.8, (MW of P_4) x (number of P_4 in compound) = 116.466

∴ (Trapping P_4 / total mass) = 116.466 / 1699.8 = 0.06851

d. MW of compound $4(C_4H_{12}N^+)$, $C_{144}H_{96}Fe_4N_{24}O_{36}S_{12}{}^{4-}$, $0.75(P_4)$, $38.5(H_2O)$ = 4429.125, (MW of P_4) x (number of P_4 in compound) = 92.925

∴ (Trapping P_4 / total mass) = 92.925 / 4429.125 = 0.02098

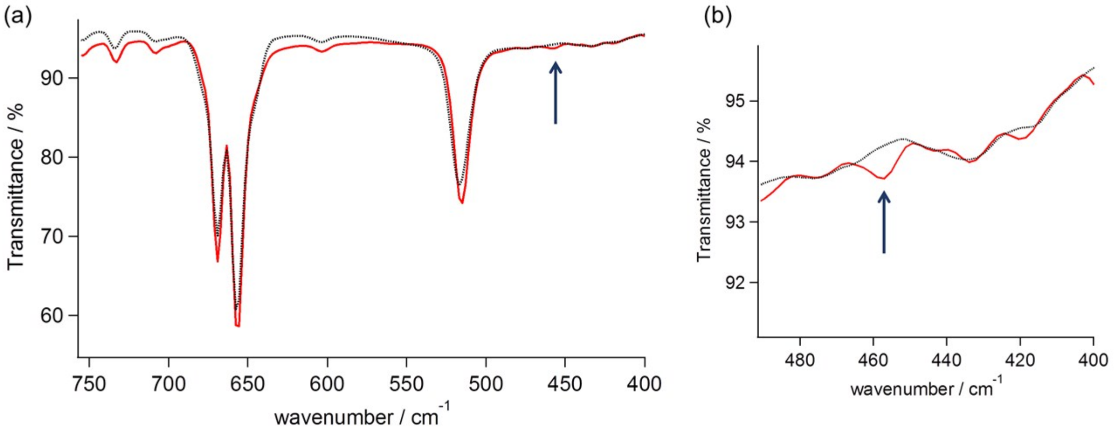

Figure S7 IR spectra (KBr pellet) of powder crystalline P_4@network **1** (red) and (black) network **1**. (a) The IR spectra at 755 – 400 cm^{-1}. (b) The IR spectra at 490 – 400 cm^{-1}. The new band appears at 457 cm^{-1} (shown by an arrow).

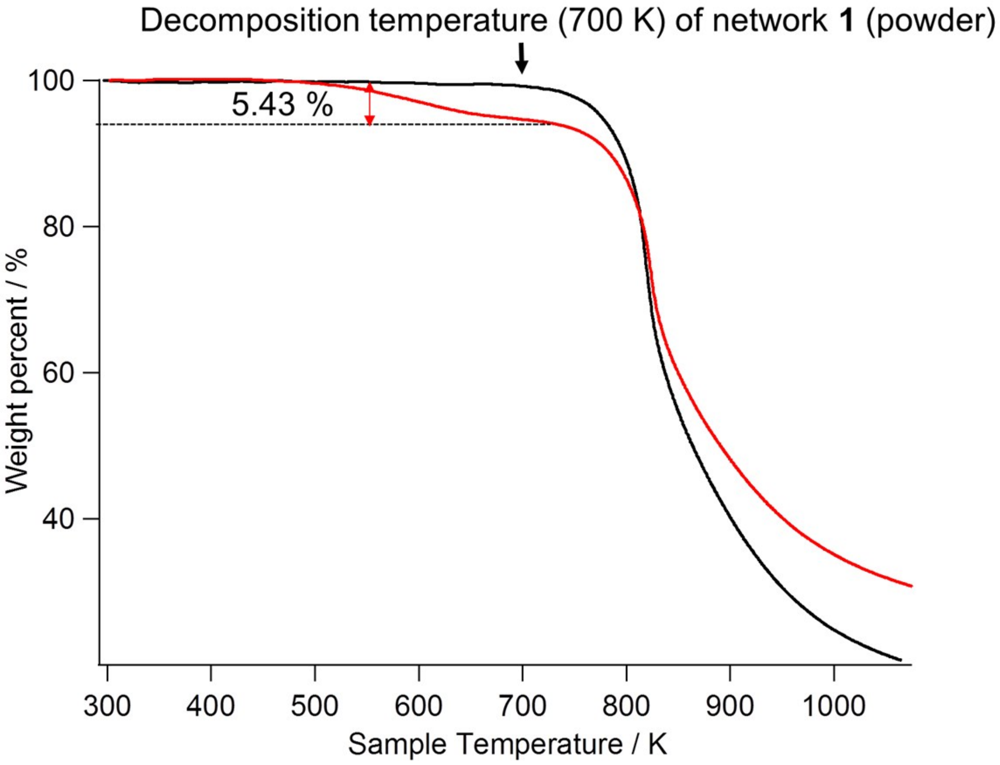

Figure S8. TG of P_4@network **1** (powder) (red) and network **1** (powder) (black): First weight decreasing occurs above 420 K. Before reaching decomposition temperature of network, 5.43 % weight decreases.

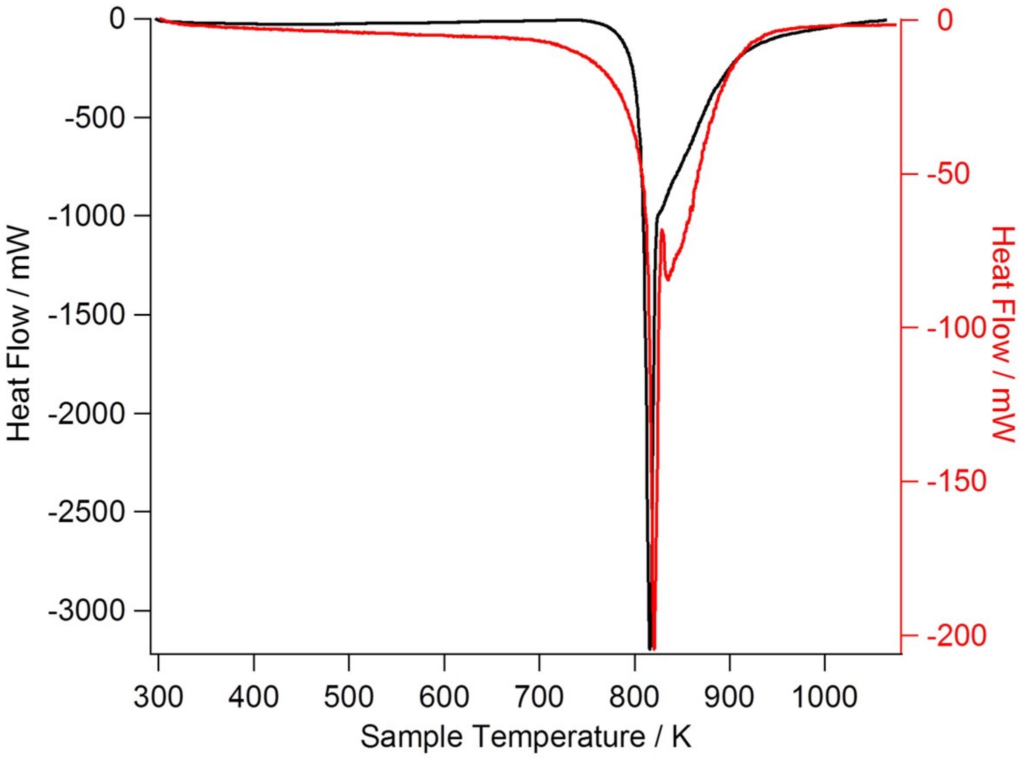

Figure S9. DSC plots of network P_4@network **1** (powder) (red) and network **1** (black).

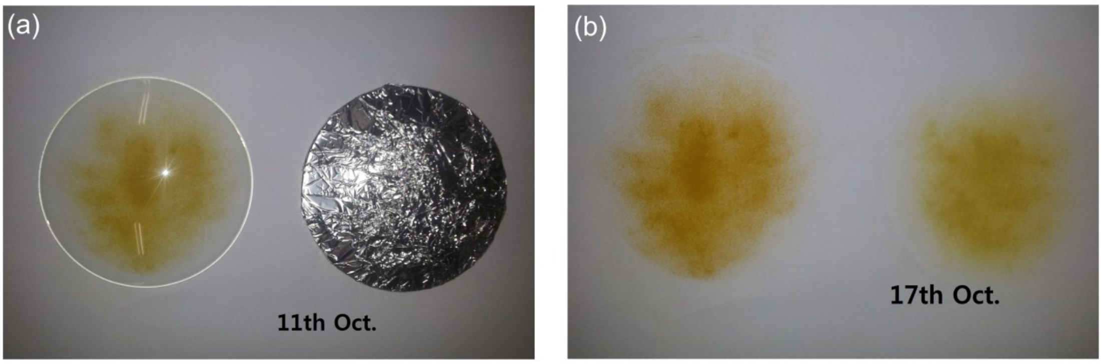

Figure S10. (a) Powder crystalline P_4@network **1** covered by transparent glass (left) or aluminium foil (right) under visible light; (b) the colour of network P_4@network **1** after 6 days visible light exposure; the powder covered only by glass (left) changed from pale green to yellow, in contrast, the powder covered by aluminium foil (right) did not change.

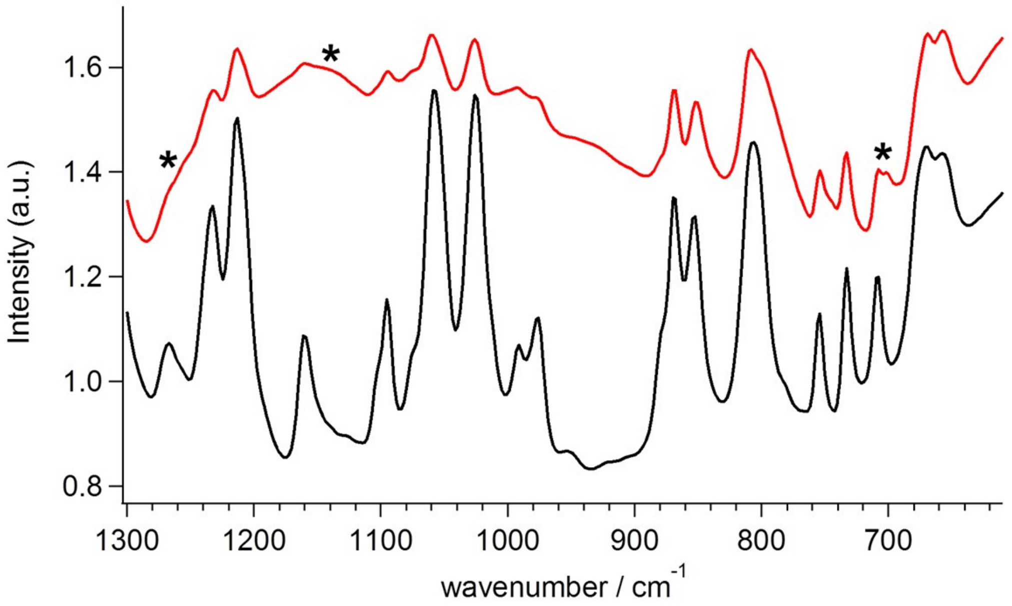

Figure S11. Microscopic-IR spectra (reflectance mode) of P_4@network **1** exposed by visible light for 6 days (red) and initial state of P_4@network **1** (black). The new band appears at 1255, 1140, and 700 cm^{-1} (marked by asterisk).

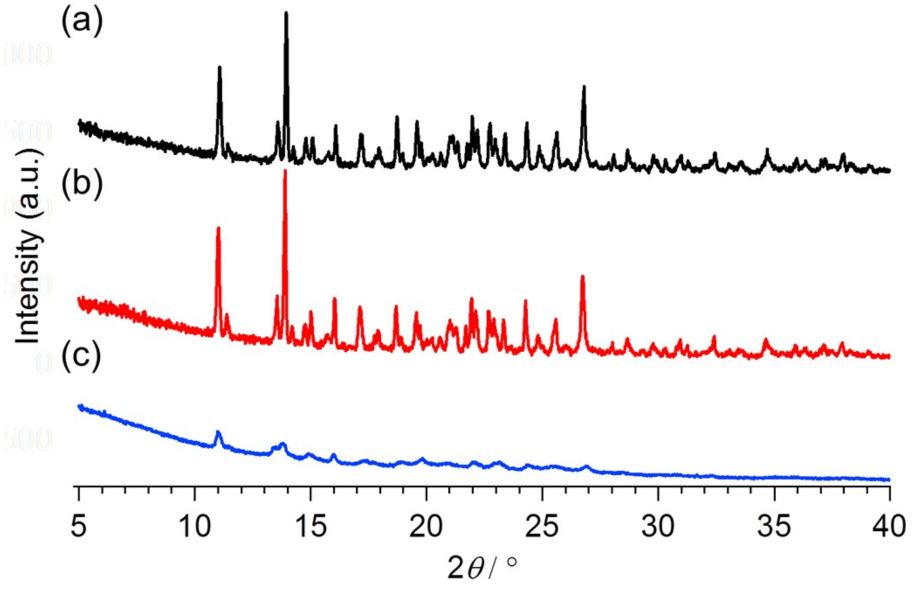

Figure S12. XRPD patterns of light exposure experiment for 3 months:

(a) P_4@network **1**, (b) P_4@network **1** under dark in air, (c) P_4@network **1** under visible light in air. The crystallinity of light exposed network deteriorated.

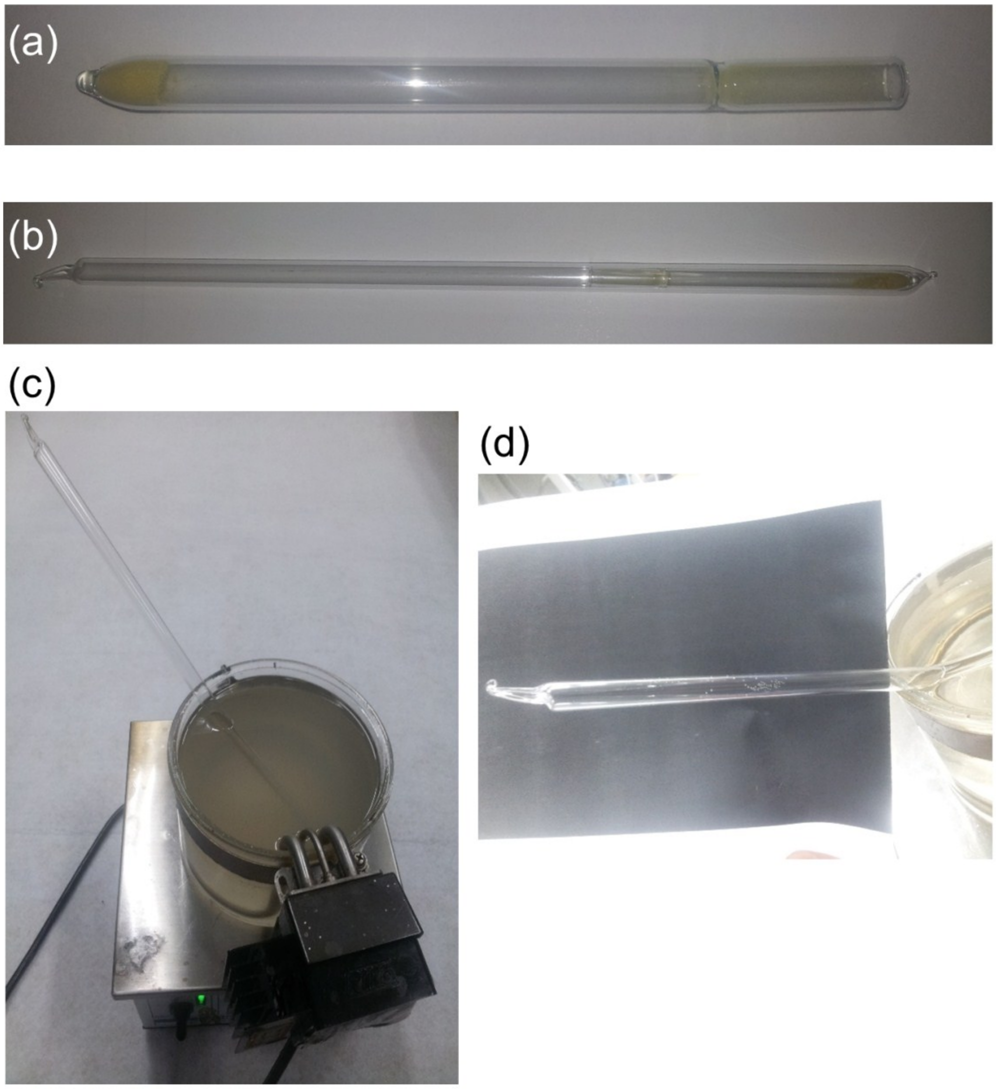

Figure S13. Experimental set up for P_4 extraction by heating: (a) P_4@network **1** (powder) in a pipet; (b) whole glass sealed under reduced pressure; (c) glass immersed in an oil bath; (d) colourless, waxy material on the opposite side of heated part.

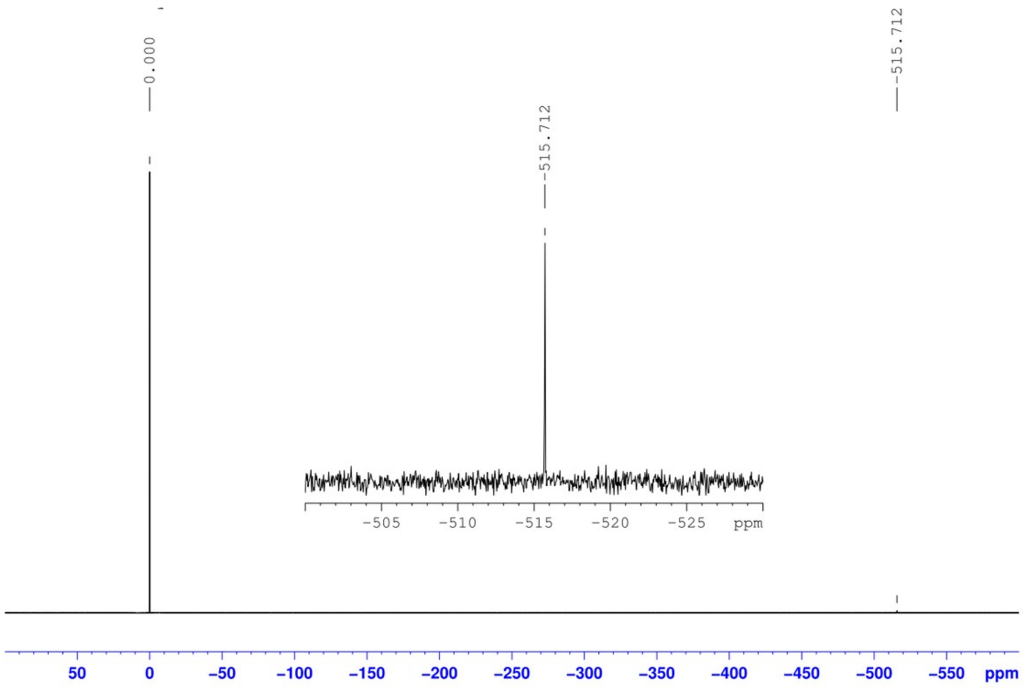

Figure S14. ^{31}P NMR (500MHz, H_3PO_4) of the waxy material dissolved in *d_6*-DMSO.

Table S4. Time and temperature dependent ^{31}P NMR peak intensity change of P_4 (*vs* Triphenylphosphine) during extraction.

Temperature / K	Time / min.	P_4 position / ppm	Ratio of integration intensity**; P_4/PPh_3
423	5	-523.18	0.962
	15	-523.19	1.457
300	5	-523.23	0.093
	15	-523.24	0.106

* Chemical shift of Triphenylphosphine (used as internal standard) was determined as -5.247 ppm vs. H_3PO_4 in d_5-nitrobenzene

** Integration intensities were calculated using the range ±0.06 ppm from peak tops.

Table S5. Activation and regeneration of P_4 by heating under reduced pressure.

	Trapping and activation	**First**	**Second**	**Third**
1	Initial P_4 weight percent in P_4@network **1** (%)(from EA)	6.44[a]	6.51[b]	6.44[c]
2	Weight of P_4@network **1** (mg) : before activation	257.59	160.92	94.09
3	Weight of P_4@network **1** (mg) : after activation	243.67	153.08	89.90
4	Weight decrease (mg)*	13.92	7.84	4.19
5	Weight decrease (%)**	5.40	4.8	4.45
6	P_4 extraction ratio***	0.839	0.737	0.691

*(line 3 – line 2) : it is corresponding to the amount of extracted P_4.

**(line 4 / line 2)×100

***(line 5 / line 1) : it shows how efficiently the P_4 was extracted.

Elemental analysis

First P_4 trapping[a]

Found : C, 25.54; H, 1.544; N, 9.925.

Calc. for $C_{36}H_{24.24}I_6N_{12}O_{0.12}P_{3.52}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.88}(H_2O)_{0.12}]\}$: C, 25.53; H, 1.44; N, 9.93; P, 6.44.

Second P_4 trapping[b]

Found : C, 25.51; H, 1.486; N, 9.967.

Calc. for $C_{36}H_{24.22}I_6N_{12}O_{0.11}P_{3.56}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.91}(H_2O)_{0.11}]\}$: C, 25.52; H, 1.44; N, 9.92; P, 6.51.

Third P_4 trapping[c]

Found : C, 25.54; H, 1.509; N, 9.885.

Calc. for $C_{36}H_{24.24}I_6N_{12}O_{0.12}P_{3.52}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.88}(H_2O)_{0.12}]\}$: C, 25.53; H, 1.44; N, 9.93; P, 6.44.

Table S6. Extraction and regeneration of P_4 by immersing in hot nitrobenzene.

	Trapping and extraction	First	Second	Third
1	Initial P_4 weight percent in P_4@network **1** (%)(from EA)	6.16[a]	5.60[c]	5.88[e]
2	P_4 weight percent in network after extraction (%)(from EA)	1.45[b]	1.38[d]	1.89[f]
3	P_4 decrease (%)*	4.71	4.22	3.99
4	P_4 extraction ratio**	0.765	0.754	0.679

*(line 1 – line 2)

**(line 3 / line 1) : it shows how efficiently the P_4 was extracted.

Elemental analysis

(For extracted samples, the sample were washed with diethyl ether to remove surface nitrobenzene)

First P_4 trapping[a]

Found : C, 25.61; H, 1.555; N, 9.945.

Calc. for $C_{36}H_{24.24}I_6N_{12}O_{0.12}P_{3.52}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.84}(H_2O)_{0.16}]\}$: C, 25.60; H, 1.45; N, 9.95; P, 6.16.)

First P_4 extraction[b]

Found : C, 28.74; H, 1.738; N, 10.596.

Calc. for $C_{40.8}H_{28}I_6N_{12.8}O_{1.6}P_{0.8}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.2}(C_6H_5NO_2)_{0.8}]\}$: C, 28.73; H, 1.65; N, 10.51; P, 1.45.

Second P_4 trapping[c]

Found : C, 25.73; H, 1.499; N, 9.886.

Calc. for $C_{36}H_{24.48}I_6N_{12}O_{0.24}P_{3.04}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.76}(H_2O)_{0.24}]\}$: C, 25.73; H, 1.47; N, 10.00; P, 5.60.

Second P_4 extraction[d]

Found : C, 28.76; H, 1.788; N, 10.451.

Calc. for $C_{40.86}H_{28.05}I_6N_{12.81}O_{1.62}P_{0.76}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.19}(C_6H_5NO_2)_{0.81}]\}$: C, 28.77; H, 1.66; N, 10.52; P, 1.38.

Third P_4 trapping[e]

Found : C, 25.66; H, 1.511; N, 10.004.

Calc. for $C_{36}H_{24.4}I_6N_{12}O_{0.2}P_{3.2}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.8}(H_2O)_{0.2}]\}$: C, 25.66; H, 1.46; N, 9.98; P, 5.88.

Third P_4 extraction[f]

Found : C, 28.46; H, 1.717; N, 10.369.

Calc. for $C_{40.44}H_{27.7}I_6N_{12.74}O_{1.48}P_{1.04}Zn_3$: $\{[(ZnI_2)_3(TPT)_2(P_4)_{0.26}(C_6H_5NO_2)_{0.74}]\}$: C, 28.48; H, 1.64; N, 10.46; P, 1.89.

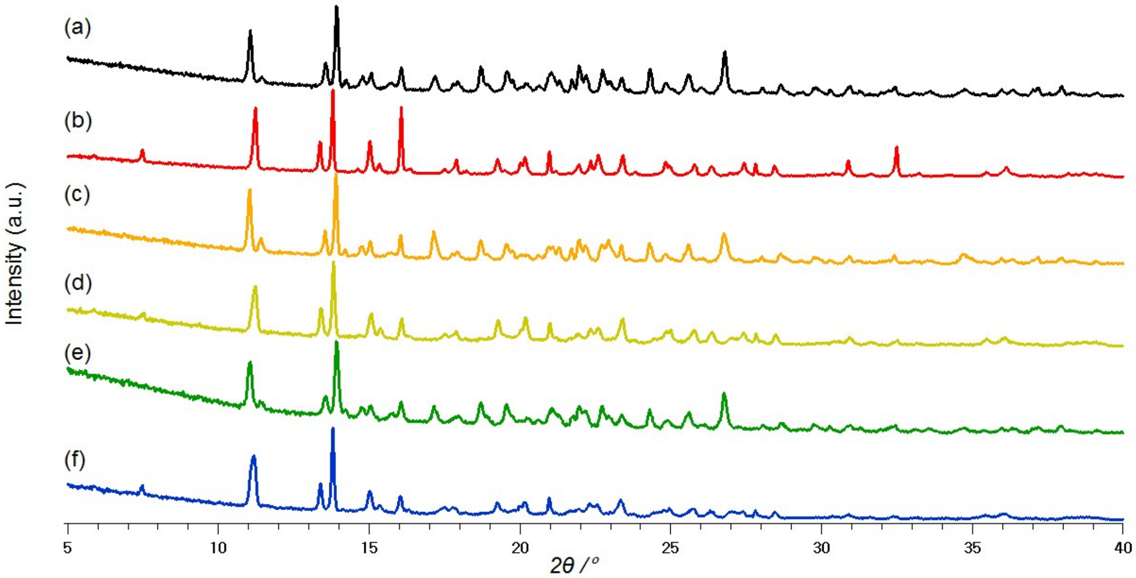

Figure S15. XRPD patterns of crystalline powder network by trapping/extraction of P_4 with heating (λ = 1.54056 Å, Cu $K_{\alpha 1}$): (a) after first P_4 trapping to network **1**, (b) after first activation (extraction), (c) after second P_4 trapping, (d) after second activation (extraction), (e) after third P_4 trapping**,** (f) after third activation (extraction).

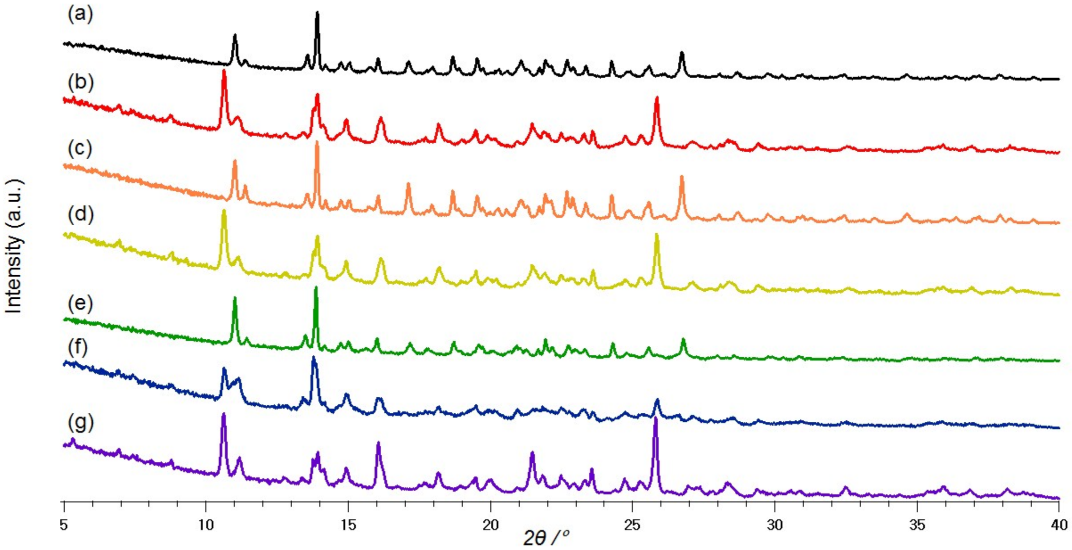

Figure S16. XRPD patterns of crystalline powder network by trapping/extraction of P_4 in hot nitrobenzene (λ = 1.54056 Å, Cu $K_{\alpha 1}$): (a) after first P_4 trapping to network **1**, (b) after first extraction of P_4, (c) after second P_4 trapping, (d) after second extraction, (e) after third P_4 trapping**,** (f) after third extraction (g) nitrobenzene-trapping network **1** : for comparison with (d), (e) and (f), 5mg of empty powder crystalline network **1** was immersed in 2mL of nitrobenzene for 5 h, and network was washed by diethyl ether.

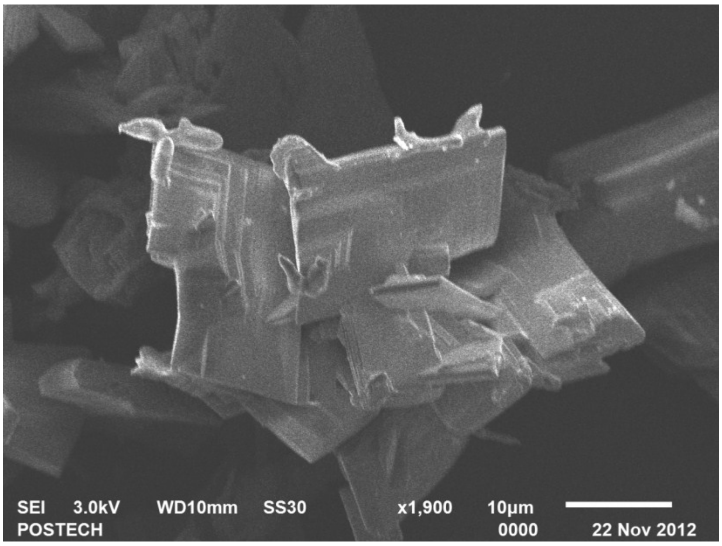

Figure S17. SEM of the powder crystalline network **1**, indicating maximum size is around 20 μm.

References for ESI

[S1] Anderson, L. H.; Anderson, S.; Sanders, M. K., *J. Chem. Soc., Perkin Trans. 1.*1995, 2231-2245.

[S2] T. Kojima, W. Choi and M. Kawano, *Chem. Commun.*, 2014, **50**, 13793-13796.

[S3] K. Ohara, J. Martí-Rujas, T. Haneda, M. Kawano, D. Hashizume, F. Izumi, and M. Fujita, *J. Am. Chem. Soc.* 2009, **131**, 3860–3861.