Supporting Information

Materials

Silver hexafluorophosphate (Aldrich) and o-bis(diphenylphosphino)benzene (Wako Chemical Co. Ltd.) was purchased and used without purification. Potassium bis(diphenylthiophosphinyl)imide ($KdppaS_2^-$) was synthesized by the literature method.[1]

Preparation of PMMA film dispersing 1b

Polymethylmethacrylate (0.20g) was dissolved in $CHCl_3$ (5ml) at 40ºC and then complex **1b** (10 mg) was added to the solution and the mixture was stirred vigorously. After the solution was cooled and poured into glass Petri dish (ϕ 60 mm), all solvent in solution was removed by slow evaporation. Upon measurement, a part of the film peered from the dish was used.

General procedure for measurements

Elemental analyses were performed on the Eurovector EUROEA3000-Dual CHN Analyzer. The absorption spectra of the solid samples were recorded on a Shimadzu UV-3100 spectrophotometer equipped with an integrating sphere. The emission and excitation spectra of the complexes were recorded on a Shimadzu RF-5000 fluorometer The TG (thermogravimetry) and DTA (differential thermal analysis) measurements were performed on a Shimadzu DTG-50. About 20 mg of sample was heated in a platinum crucible at a rate of 1ºC·min^{-1} in the temperature range 25–180ºC, followed by heating at a rate of 2ºC·min^{-1} to 250ºC to observe thermal decomposition of the sample.

Powder X-ray diffraction measurements were performed over 2θ ranging from 5° to 80° using CuKα radiation on a Rigaku Ultima IV diffractometer equipped with a curved graphite monochromator.

X-ray crystallography.

X-ray crystallographic measurements were made on a Rigaku Saturn 70 CCD area detecter with graphite-monochromated MoKa radiation. The crystal-to-detector distance was 54.90 mm. The data were collected at a temperature of 123 K to maximum 2q value of 57.5º. 1800 oscillation images were collected and the data were processed by using the CrystalClear software.[2] Absorption corrections were made by the numerical method. The structures were solved by direct methods (SIR-2004[3]) and refined by full matrix least squares procedures (SHELXL-97 [4]). The non hydrogen atoms are refined anisotropically and the positions of all hydrogen atoms were fixed at calculated positions. All calculations were performed by using the CrystalStructure crystallographic software package.[5]

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 738876 and 738877 for **1b** and **2**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK;

Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

[1] I. Haidac, I. Silaghi-Dumitrescu, *Coord. Chem. Rev.*, **1986**, 74, 127.

[2] CrystalClear, Area detector Processing Software, Rigaku and Molecular Structure

Corp., 2000.

[3] SIR-2004: M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, P. Polidori, R. Spagna, *J. Appl. Crystallogr.*, **2005**, 38, 381-388.

[4] G. M. Sheldrick, SHELXL-97, Program for Crystal Determination and Refinement, University of Göttingen, Germany, 1997.

[5] CrystalStructure, ver.3.80: Single Crystal Structure Analysis Software, Molecular Structure Corporation.

Table S1. Crystallographic data

	Blue form (**1b**)	Green form (**2**)
Formula	$C_{54}H_{44}NP_4S_2Ag$	$C_{54}H_{44}NP_4S_2Ag$
Fw	1002.83	1002.83
Temperature (K)	123	123
Crystal size	0.25x0.25x0.15	0.40x0.15x0.08
Crystal system	triclinic	monoclinic
Space group	P-1 (#2)	$P2_1/c$ (#14)
a (Å)	11.445 (2)	19.6934 (10)
b (Å)	13.553 (2)	9.5780 (5)
c (Å)	16.038 (3)	25.6866 (15)
α (°)	76.752(5)	90
β (°)	82.344(6)	96.972(1)
γ (°)	73.936(5)	90
V ($Å^3$)	2320.5 (7)	4809.3 (4)
Z	2	4
D_{calc} (g/cm^3)	1.435	1.385
μ (Mo$K\alpha$/ cm^{-1})	7.01	6.75
reflections colected	21470	43850
Unique reflections	9762	10810
Rint	0.0185	0.501
$R_1(I>2.0\sigma(I))$	0.0293	0.0633
wR_2(all data)	0.0727	0.1024
GOF	1.046	1.285
Diff. peak and hole (e-/$Å^3$)	1.243; -0.451	1.169; -0.434

Fig. S1 Crystals of **1b** (left) and **2** (right) irradiated with UV-light.

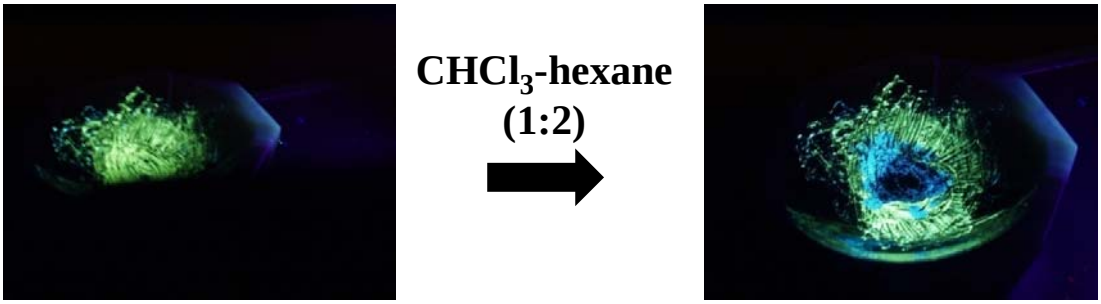

Fig. S2 Emission color change upon treatment of **1g** with drops of $CHCl_3$/hexane(1:2).

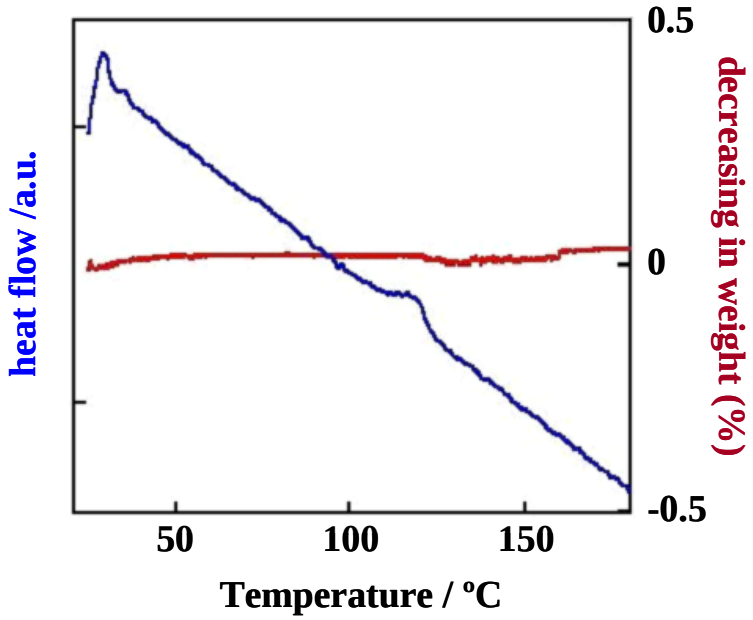

Fig. S3 DTA/TG plot for **1g** ranging from 25 to 180 ºC

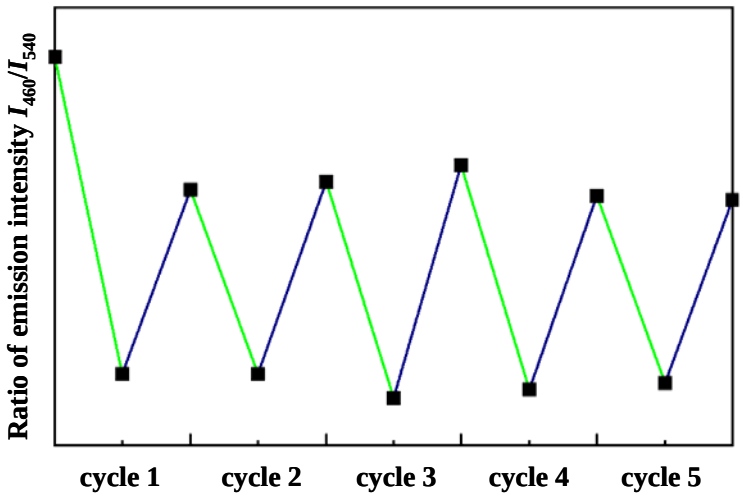

Fig. S4 Ratio of emission intensity I_{460} / I_{540} on every grinding/heating cycle.

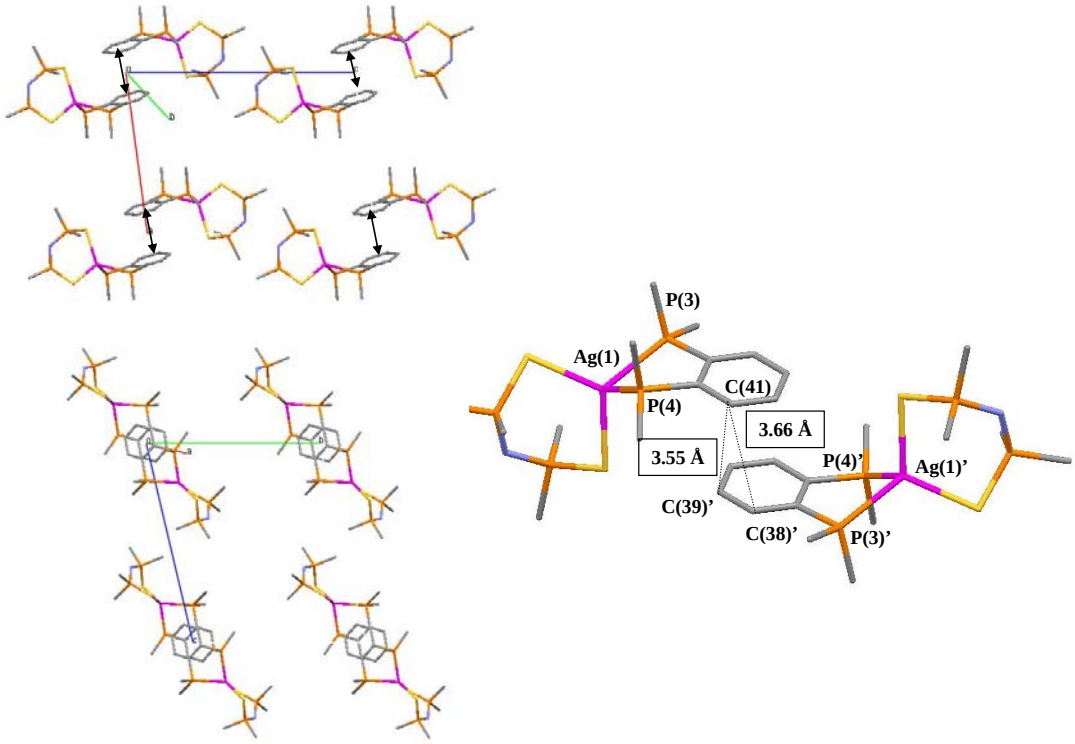

Fig. S5 Unit cell contents of **1b** projected down the *b* axis (left, above) and the *ai* axis (left, below) showing the intermolecular stacking between phenylene rings. (Carbon atoms in the terminal phenyl groups bonded to phosphorus atoms have been omitted for clarity.)

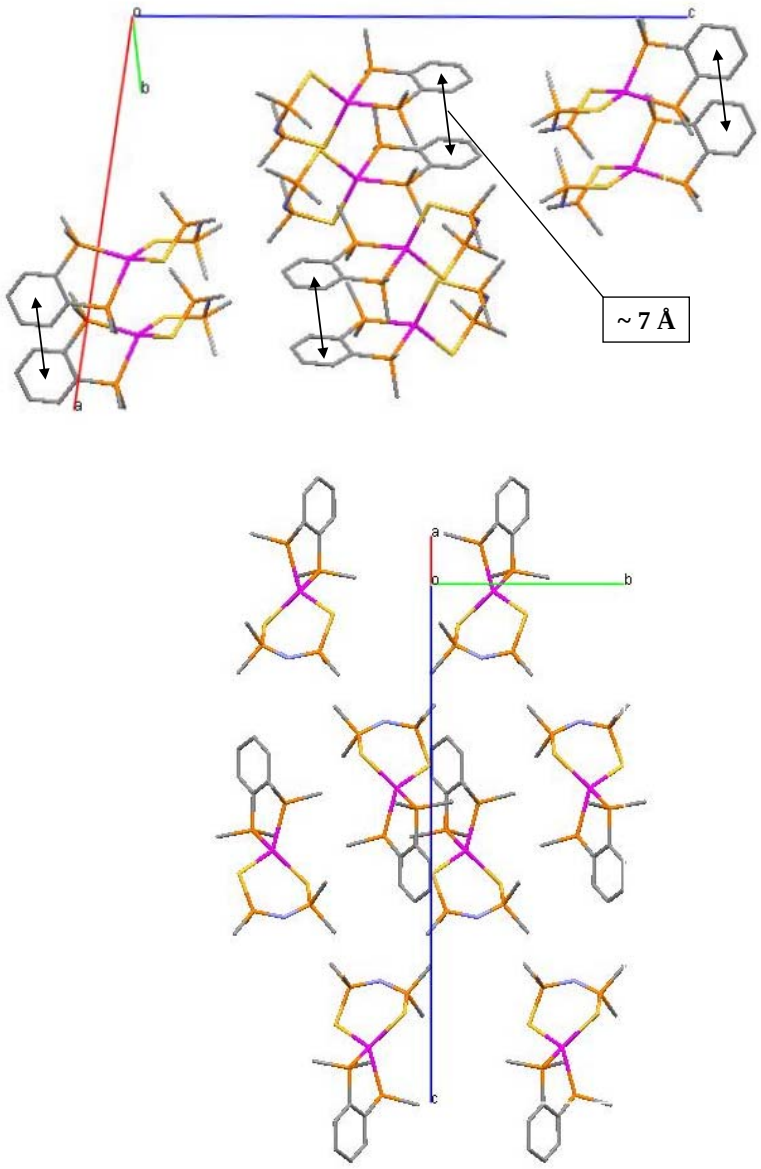

Fig. S6 Unit cell contents of **2** projected down near *b**(above) and *a**(below) showing the intermolecular stacking between phenylene rings. (Carbon atoms in the terminal phenyl groups bonded to phosphorus atoms have been omitted for clarity.)

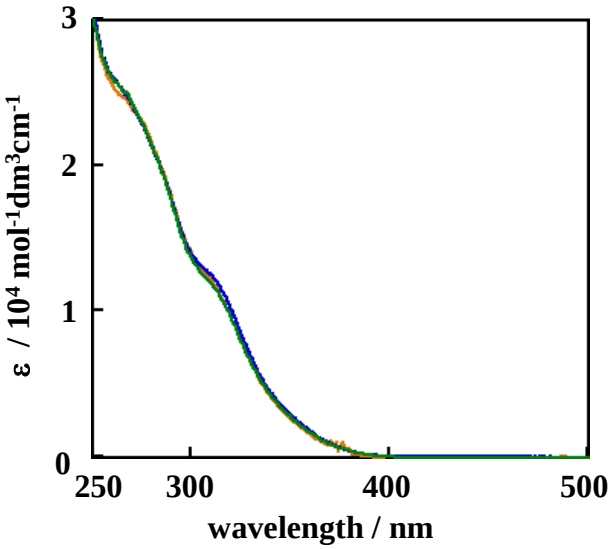

Fig. S7 Absorption spectra of **1b**(blue), **1g**(green) and **2**(orange) in CH_2Cl_2 solution.emission

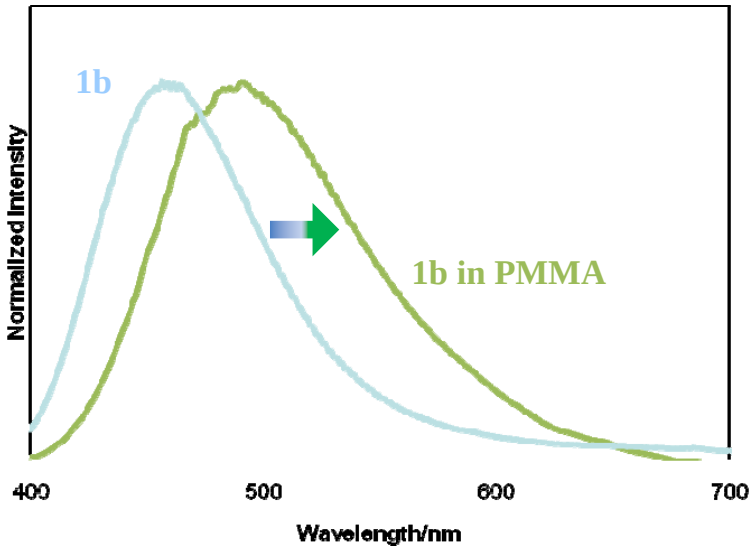

Fig. S8 Emission spectra of **1b** dispersed in PMMA film.

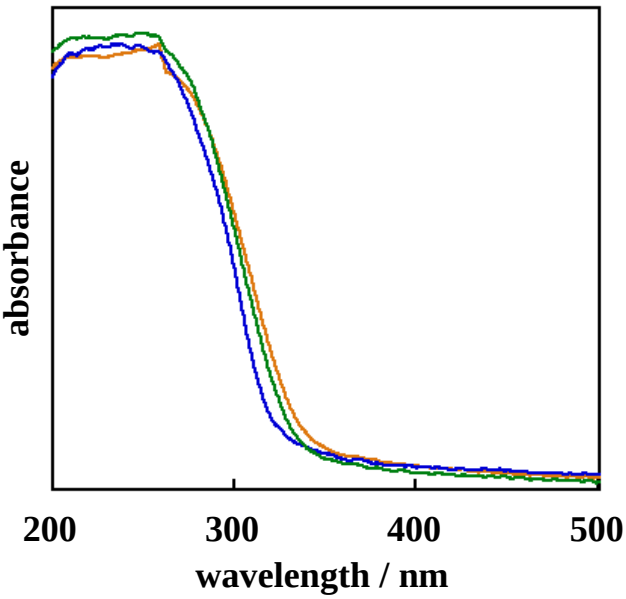

Fig. S9 Diffuse reflectance spectra of **1b**(blue), **1g**(green) and **2**(orange)

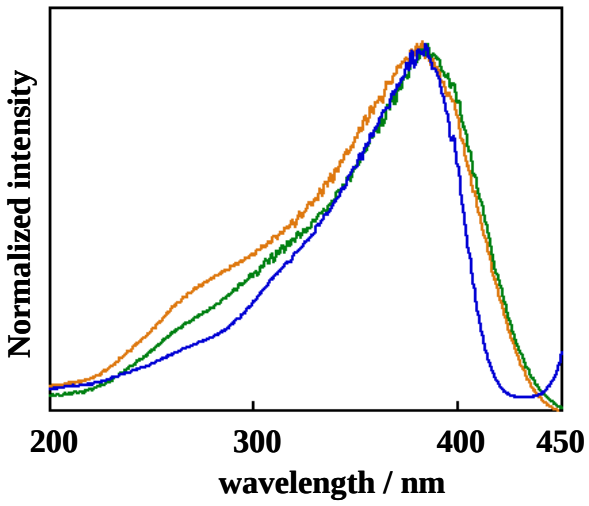

Fig. S10 Excitation spectra of **1b** (blue) observed at 458 nm, **1g** (green) observed at 518 nm and **2** (orange) observed at 520 nm.