Supplementary Information

Effect of Phosphine Ligand on the Optical Absorption/Emission Properties of Platinum-Containing Conjugated Polymers

Yu Miyagi,[a] Taichi Sotani,[a] Tatsuo Yajima,[a] Natsuhiro Sano,[b] Fumio Sanda*[a]

[a] Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan

[b] R&D Division, Nippon Chemical Industrial Co., LTD., 9-11-1 Kameido, Koto-ku, Tokyo 136-8515, Japan

*Corresponding Author. E-mail: sanda@kansai-u.ac.jp.

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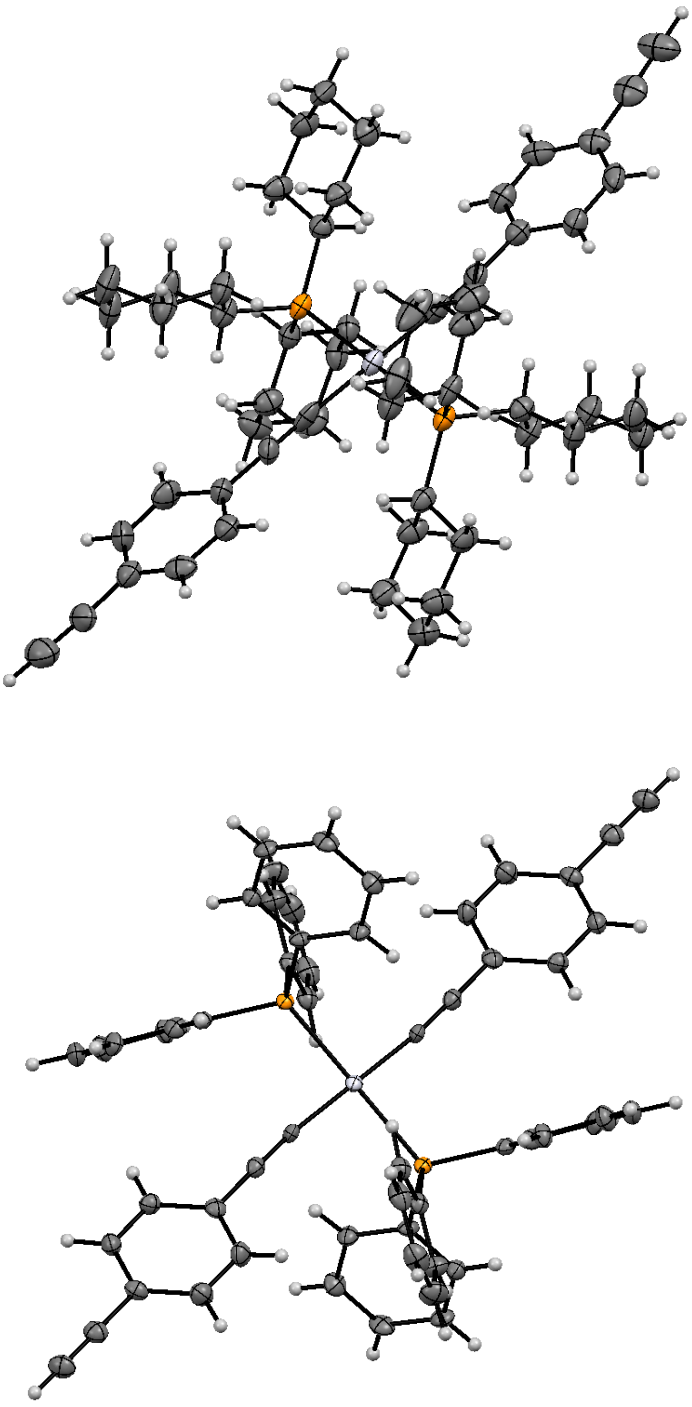

Fig. S1 ORTEP drawings of the molecular structures of **3** (top) and **4** (bottom) (50% probability ellipsoids).

Table S1 Conformation, Relative Energy and HOMO–LUMO Gap of Monomer 1[a]

dihedral angle (degree)	Pt–P average distance (Å)	relative energy (kJ/mol)	HOMO–LUMO gap (eV)
0	2.36573	3.18	3.713
10	2.36581	3.22	3.728
20	2.36511	3.32	3.766
30	2.36539	2.93	3.821
40	2.36537	2.34	3.890
50	2.36645	1.45	3.969
60	2.36668	0.75	4.050
70	2.36671	0.40	4.129
80	2.36670	0.11	4.182
90	2.36672	0.00	4.192

[a] Data corresponding to **Fig. 4**.

Table S2 Conformation, Relative Energy and HOMO–LUMO Gap of Monomer 4[a]

dihedral angle (degree)	Pt–P average distance (Å)	relative energy (kJ/mol)	HOMO–LUMO gap (eV)
0	2.37316	2.71	3.738
10	2.37372	1.69	3.738
20	2.37398	0.75	3.745
30	2.37450	0.23	3.761
40	2.37499	0.00	3.782
50	2.37515	0.07	3.811
60	2.37533	0.72	3.848
70	2.37551	1.55	3.891
80	2.37569	2.54	3.917
90	2.37578	3.12	3.943

[a] Data corresponding to **Fig. 4**.

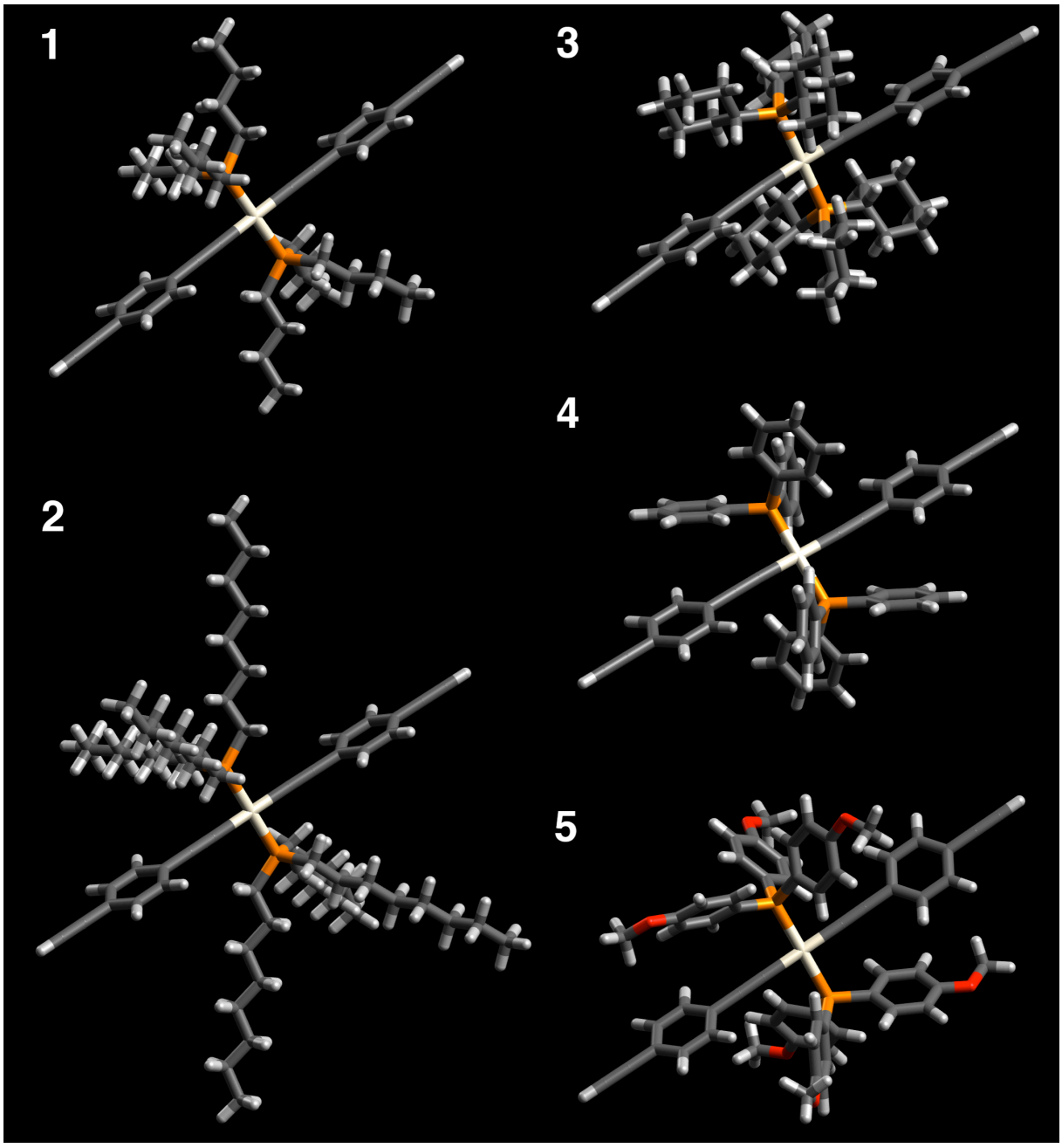

Fig. S2 Possible conformers of monomers **1**–**5**. Geometries were optimized by the DFT method [B3LYP/6-31G* (C, H, P)-LANL2DZ (Pt)].

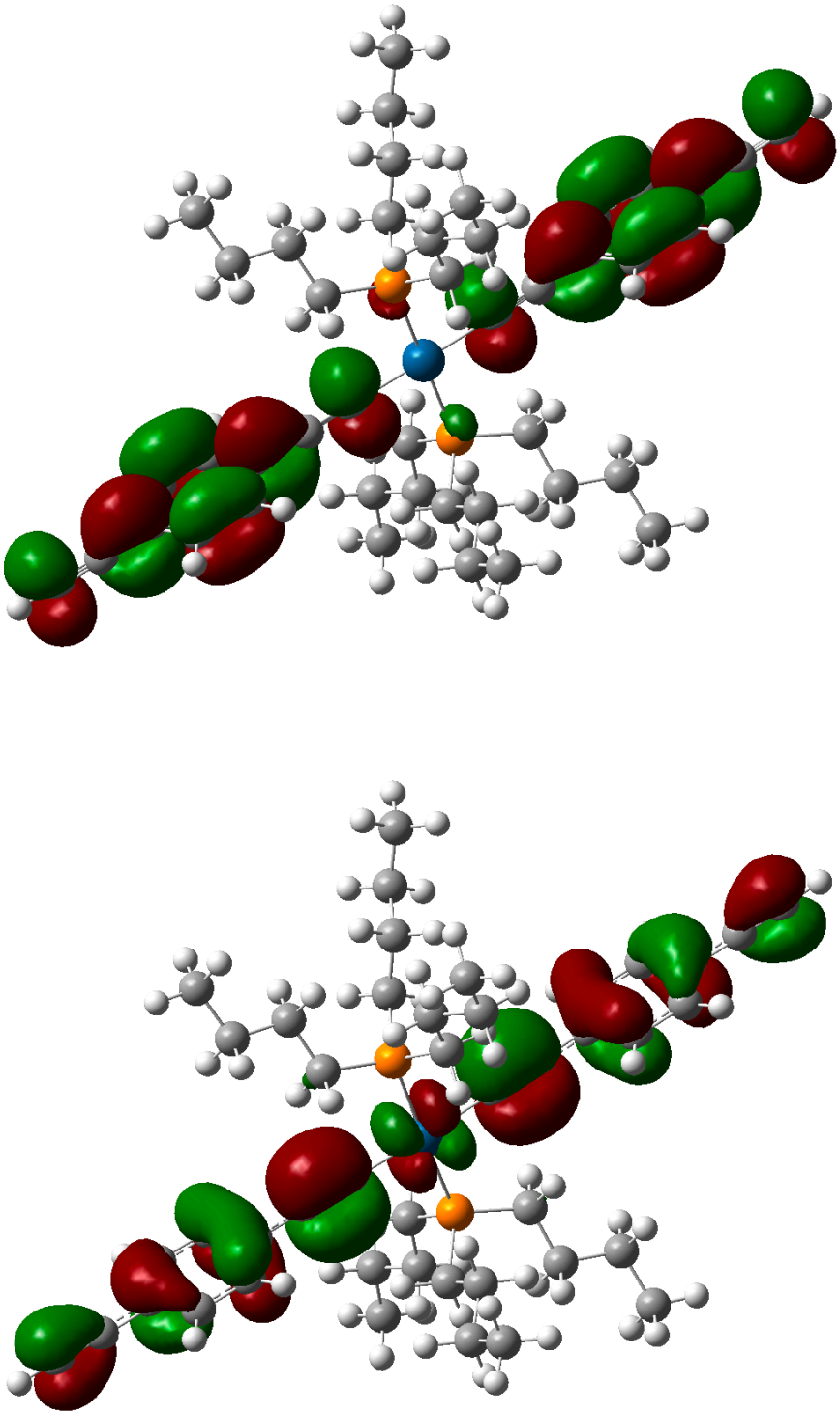

Fig. S3 LUMO (top) and HOMO (bottom) of monomer **1**. Geometries were optimized by the DFT method [B3LYP/6-31G* (C, H, P)-LANL2DZ (Pt)].

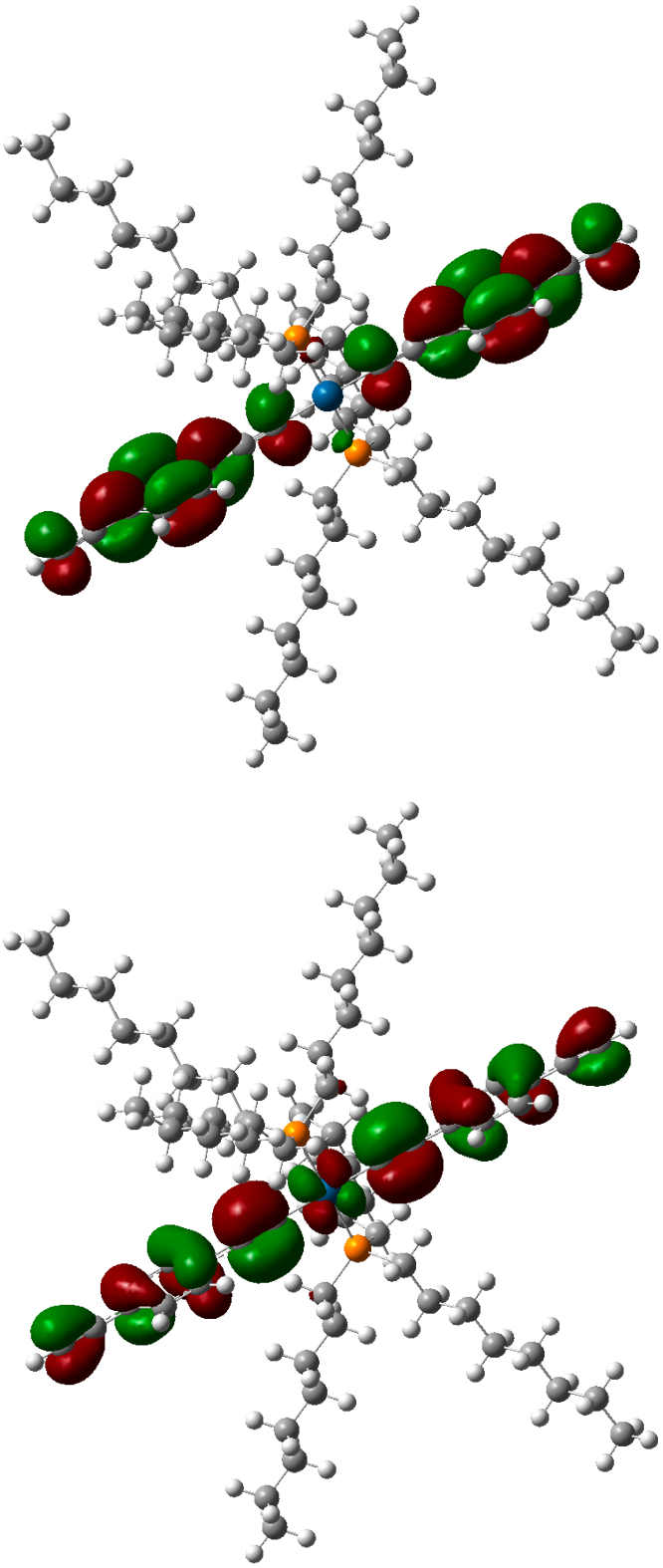

Fig. S4 LUMO (top) and HOMO (bottom) of monomer **2**. Geometries were optimized by the DFT method [B3LYP/6-31G* (C, H, P)-LANL2DZ (Pt)].

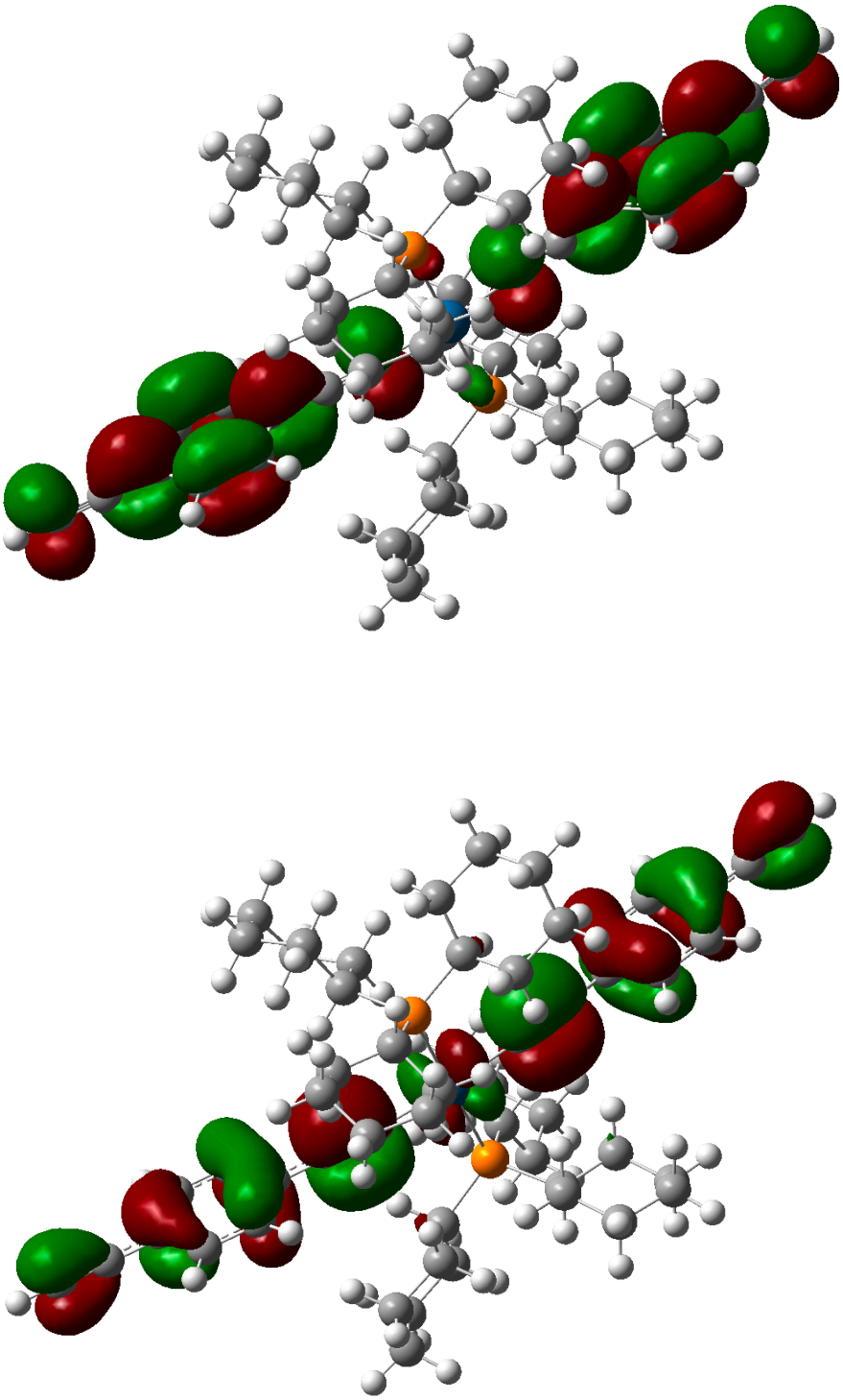

Fig. S5 LUMO (top) and HOMO (bottom) of monomer **3**. Geometries were optimized by the DFT method [B3LYP/6-31G* (C, H, P)-LANL2DZ (Pt)].

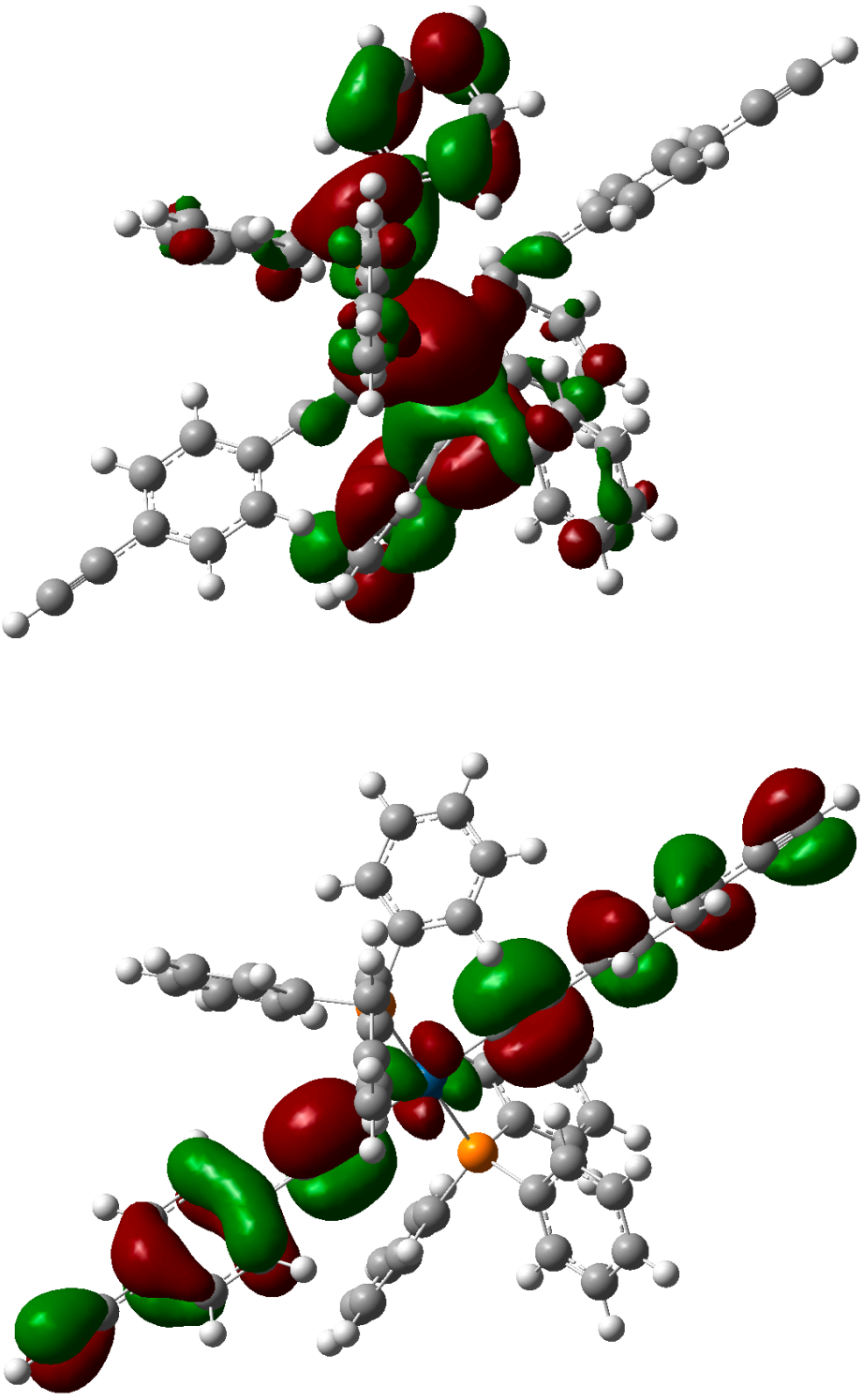

Fig. S6 LUMO (top) and HOMO (bottom) of monomer **4**. Geometries were optimized by the DFT method [B3LYP/6-31G* (C, H, P)-LANL2DZ (Pt)].

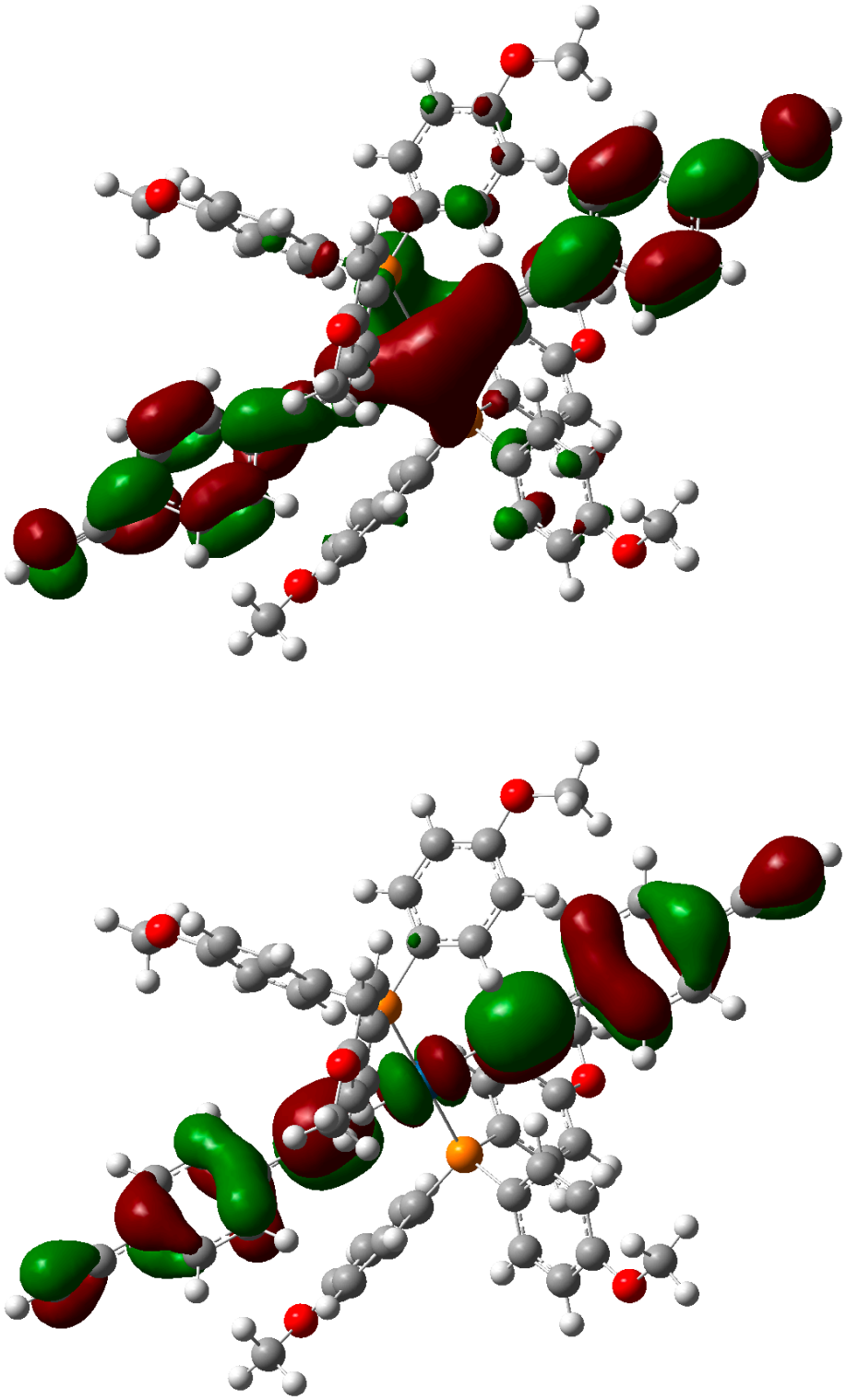

Fig. S7 LUMO (top) and HOMO (bottom) of monomer **5**. Geometries were optimized by the DFT method [B3LYP/6-31G* (C, H, P)-LANL2DZ (Pt)].

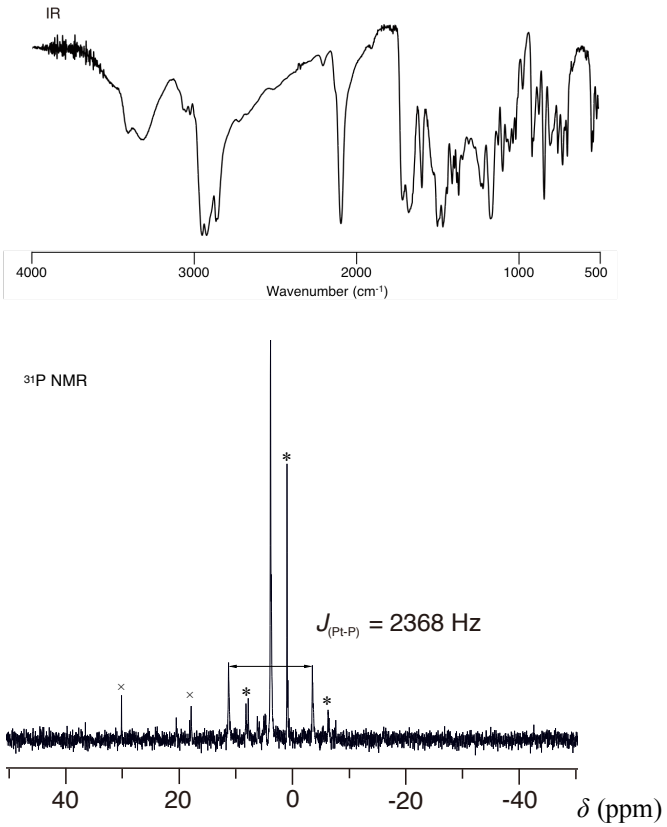

Fig. S8 IR (KBr) and ^{31}P NMR (162 MHz, measured in $CDCl_2CDCl_2$) spectra of polymer **1′**. *May be arisen from oligomers present in the polymers or from polymers with different chain length. ×Impurity.

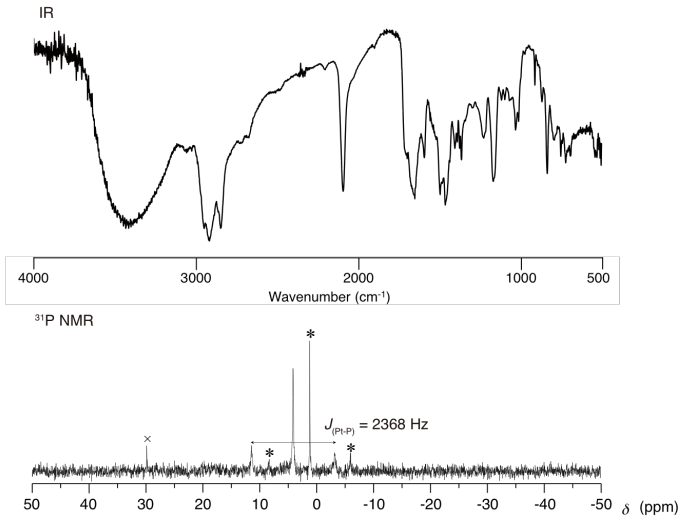

Fig. S9 IR (KBr) and ^{31}P NMR (162 MHz, measured in $CDCl_2CDCl_2$) spectra of polymer **2′**. *May be arisen from oligomers present in the polymers or from polymers with different chain length. ×Impurity.

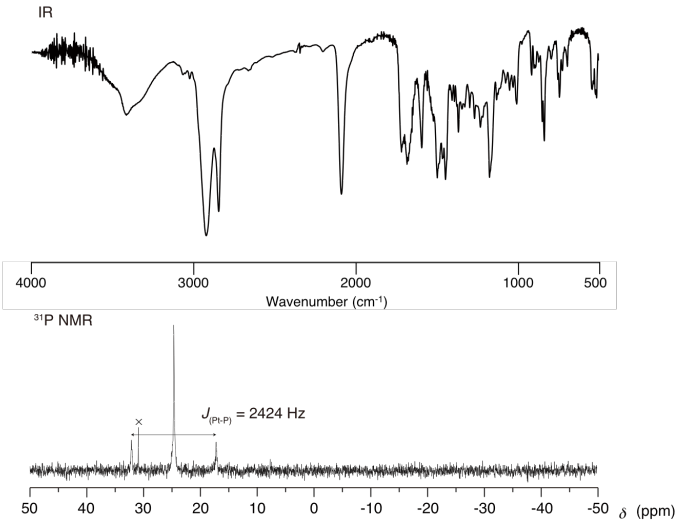

Fig. S10 IR (KBr) and ^{31}P NMR (162 MHz, measured in $CDCl_2CDCl_2$) spectra of polymer **3′**. ×Impurity.

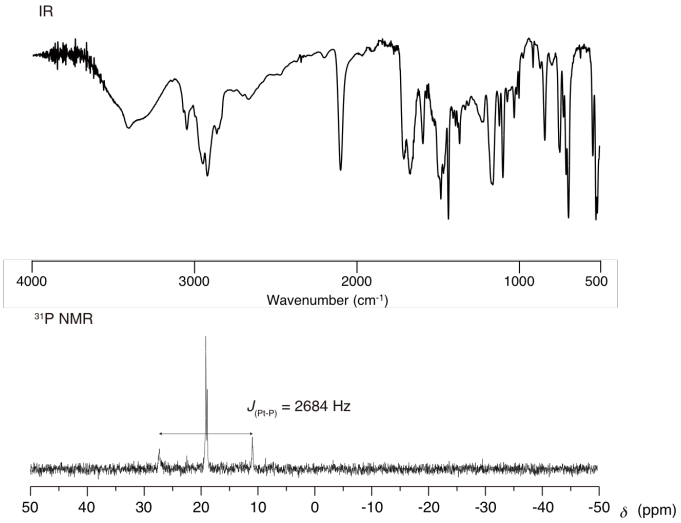

Fig. S11 IR (KBr) and ^{31}P NMR (162 MHz, measured in $CDCl_2CDCl_2$) spectra of polymer **4′**.

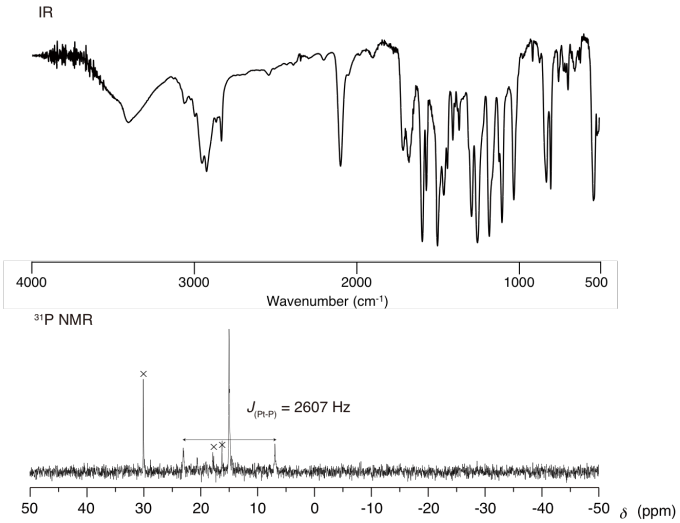

Fig. S12 IR and ^{31}P NMR (162 MHz, measured in $CDCl_2CDCl_2$) spectra of polymer **5′**. ×Impurity.

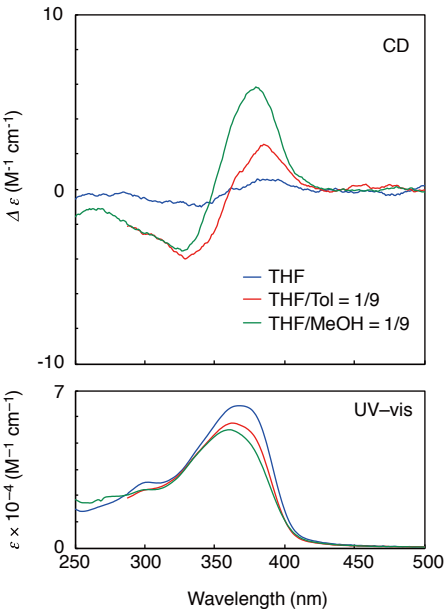

Fig. S13 CD and UV–vis spectra of polymer **1′** measured in THF, THF/toluene = 1/9 and THF/MeOH = 1/9 (c = 0.02 mM) at room temperature.

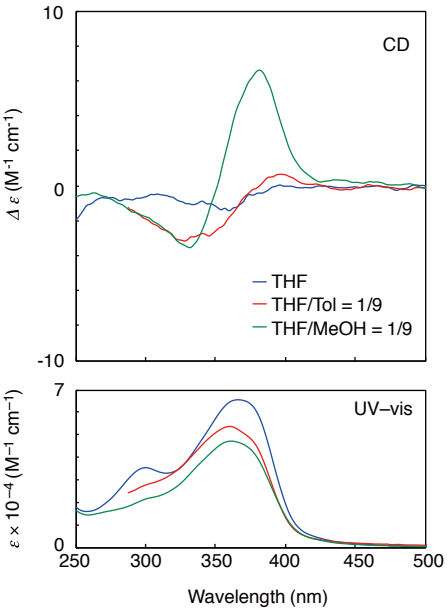

Fig. S14 CD and UV–vis spectra of polymer **2′** measured in THF, THF/toluene = 1/9 and THF/MeOH = 1/9 (c = 0.02 mM) at room temperature.

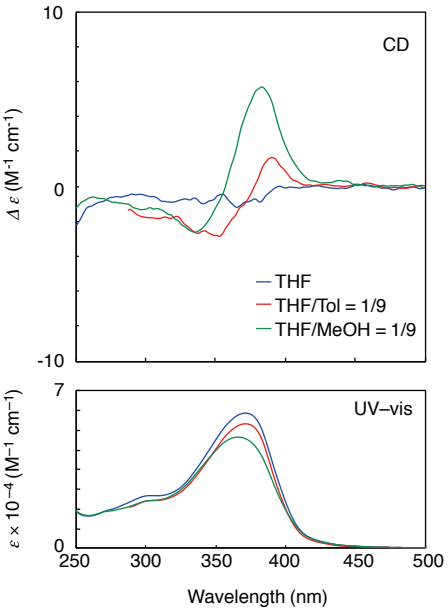

Fig. S15 CD and UV–vis spectra of polymer **3′** measured in THF, THF/toluene = 1/9 and THF/MeOH = 1/9 (c = 0.02 mM) at room temperature.

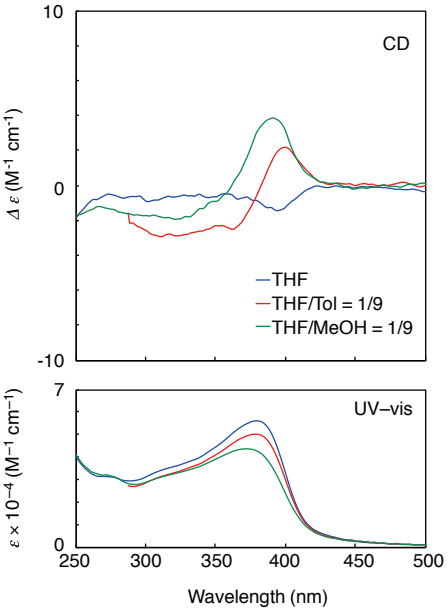

Fig. S16 CD and UV–vis spectra of polymer **4′** measured in THF, THF/toluene = 1/9 and THF/MeOH = 1/9 (c = 0.02 mM) at room temperature.

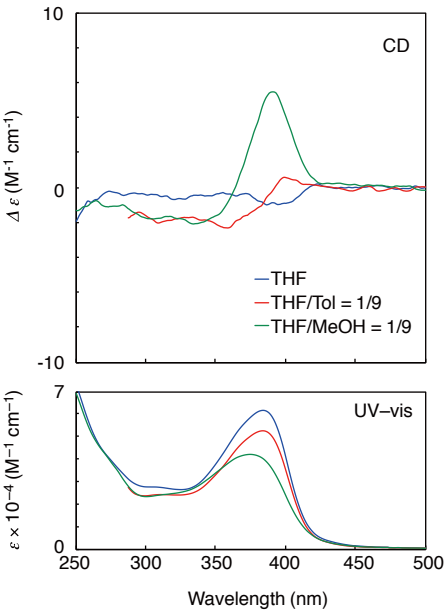

Fig. S17 CD and UV–vis spectra of polymer **5′** measured in THF, THF/toluene = 1/9 and THF/MeOH = 1/9 (c = 0.02 mM) at room temperature.

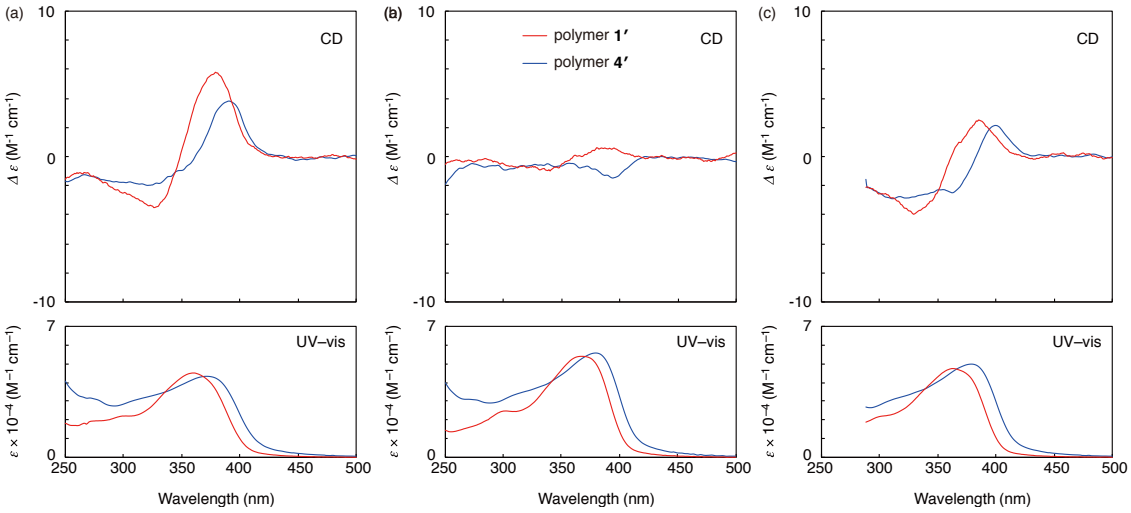

Fig. S18 CD and UV–vis spectra of polymers **1′** and **4′** measured in (a) THF/MeOH = 1/9, (b) THF and (c) THF/toluene = 1/9 at 20 °C (c = 0.02 mM).

Table S3 Absorption and emission data of monomers **1**–**5** [a]

Monomer	λ_{max} (nm)	λ_{emi} (nm)	Φ [b] (%)
1	338	492	0.043
2	338	493	0.040
3	327	494	0.046
4	360	- [c]	- [c]
5	362	- [c]	- [c]

[a] Measured in THF (c = 0.02 mM) at 25 °C. [b] Measured using anthracene as a standard (Φ = 0.27) in EtOH, excited at the λ_{max}. [c] Not determined because the intensity was very low.

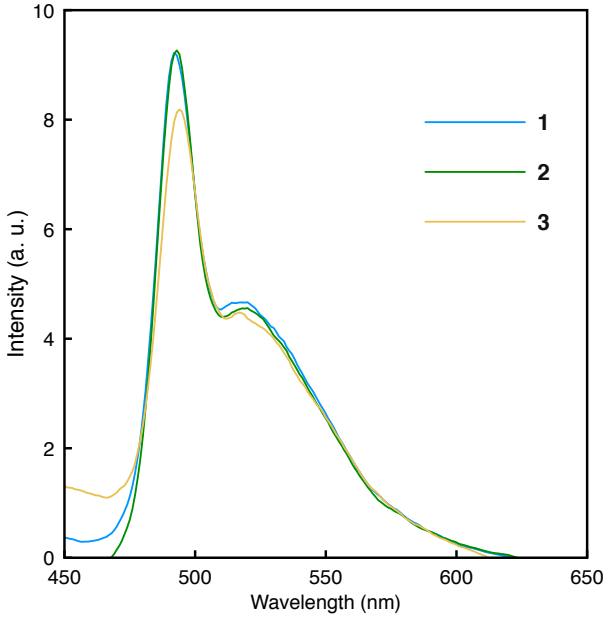

Fig. S19 Emission spectra of monomer **1**–**3** measured in THF, (c = 0.02 mM) at 20 °C, excited at the λ_{max} listed in Table S3.

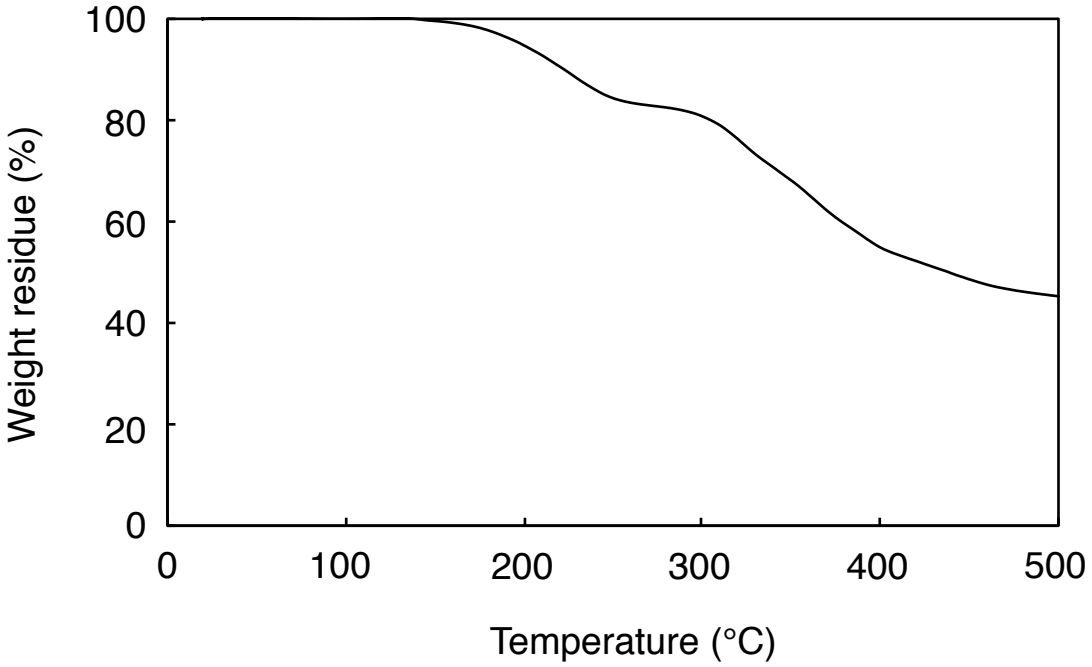

Fig. S20 TGA trace of polymer **1′** (heating rate = 10 °C/min, under N_2).

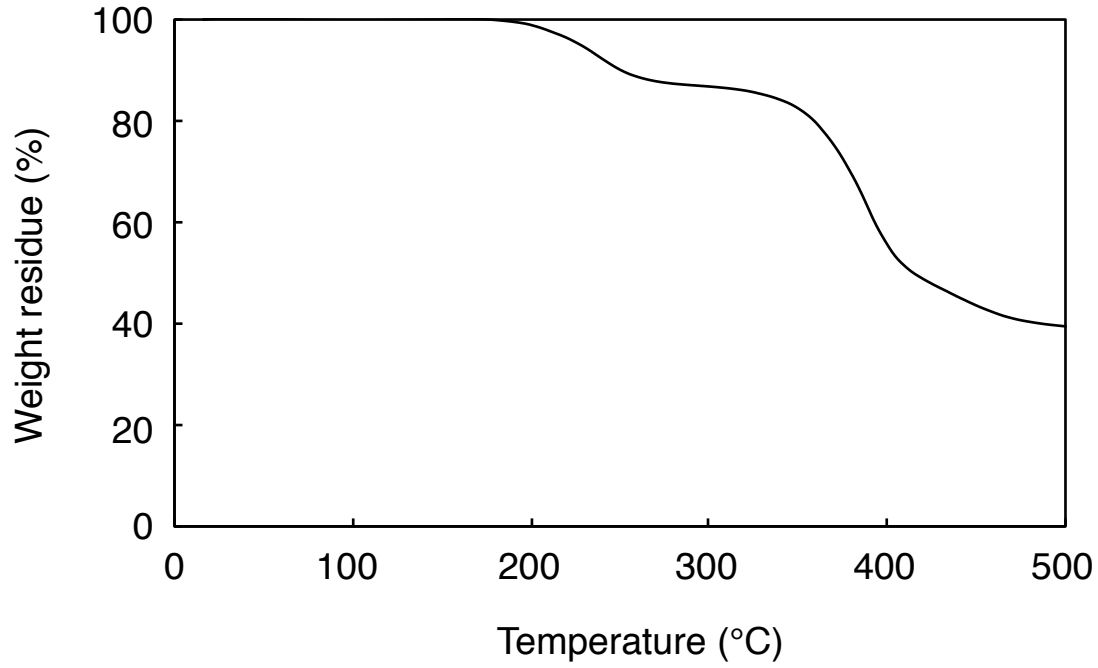

Fig. S21 TGA trace of polymer **2′** (heating rate = 10 °C/min, under N_2).

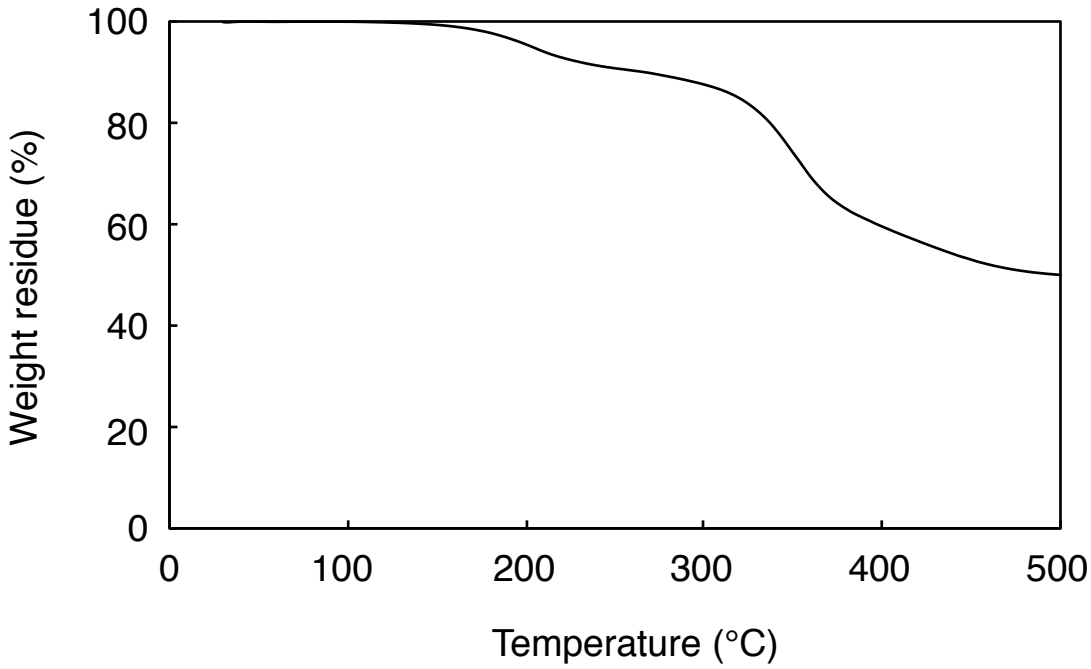

Fig. S22 TGA trace of polymer **3′** (heating rate = 10 °C/min, under N_2).

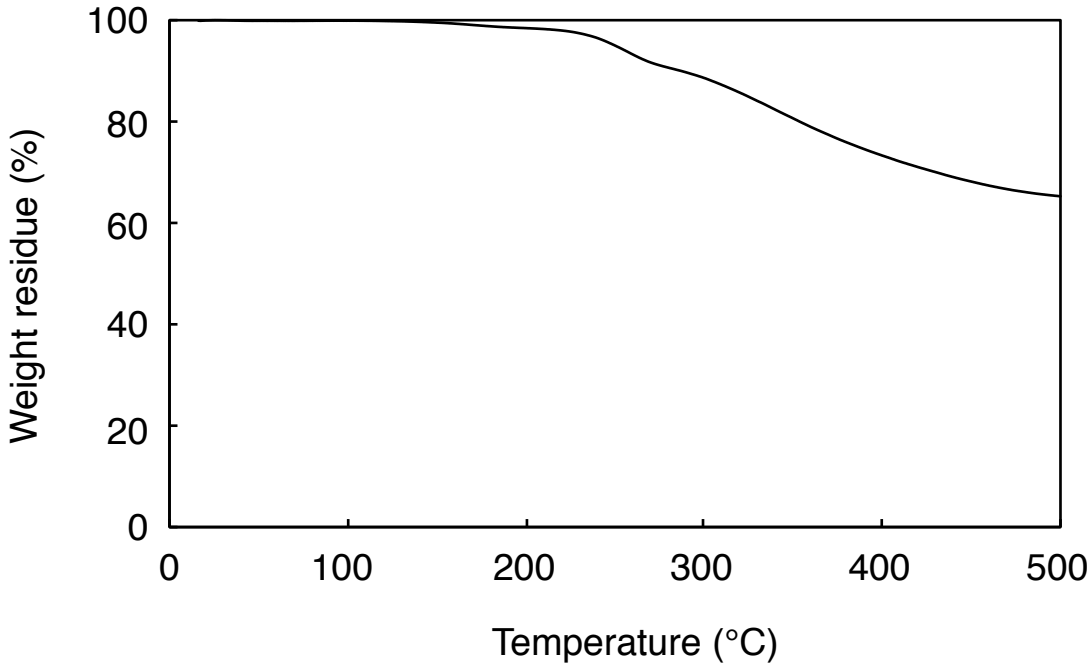

Fig. S23 TGA trace of polymer **4′** (heating rate = 10 °C/min, under N_2).

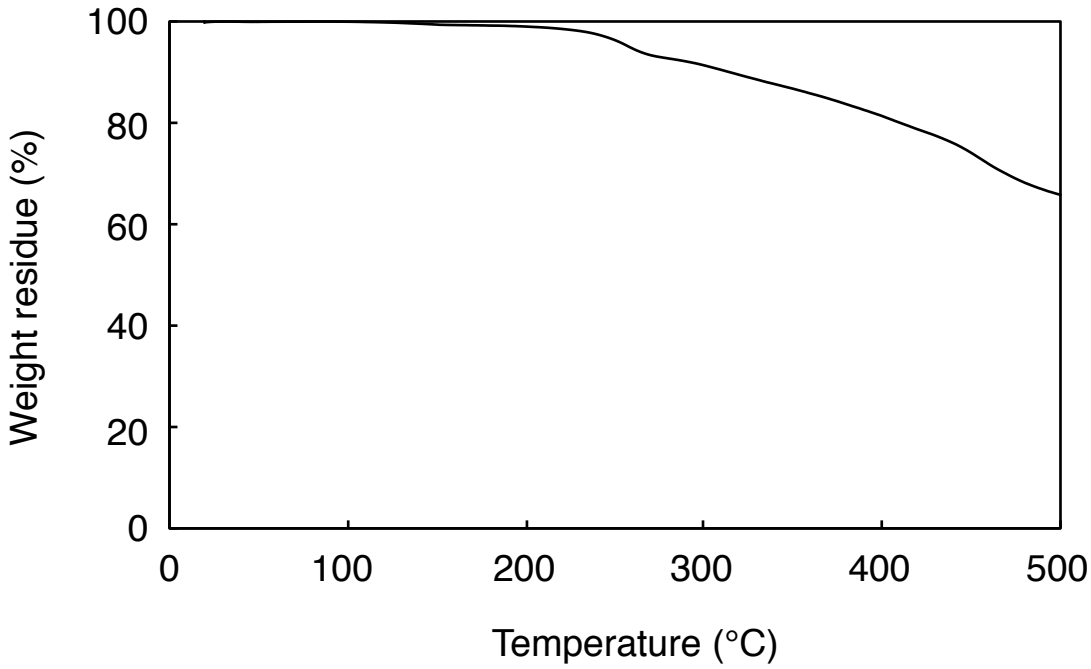

Fig. S24 TGA trace of polymer **5′** (heating rate = 10 °C/min, under N_2).