# **Electronic Supporting Information**

Chain length effect in the functionalization of polyoxometalates with  $\alpha, \omega$ -alkyldiphosphonates

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#### (1) Materials and Syntheses

All reagents were from Innochem (Beijing), TCI Co., Sigma-Aldrich, Acros, and Fisher Chemical, and used without further purification. In-house deionized water was used for sample preparation. The syntheses of  $\alpha$ , $\omega$ -alkyldiphosphonic acids: 1,4-butylenediphosphonic acid (H<sub>4</sub>L4), 1,5-pentenediphosphonic acid (H<sub>4</sub>L5), and 1,6-hexenediphosphonic acid (H<sub>4</sub>L6), were conducted following reported procedures by the Michaelis–Arbuzov reaction.<sup>1</sup> The tri-vacant Keggin precursor Na<sub>9</sub>[A- $\alpha$ -PW<sub>9</sub>O<sub>34</sub>] 7H<sub>2</sub>O was synthesized using a literature method.<sup>2</sup>

#### **1a:** $Rb_{29}Na_{15}[(A-PW_9O_{34})_8Mn^{III}_{20}(OH)_8(H_2O)_8(L6)_6]$ 92H<sub>2</sub>O, m.w. 25149.46

A sample of Mn(O<sub>2</sub>CMe)<sub>3</sub> 2H<sub>2</sub>O (0.34 g, 1.20 mmol) was suspended in a 20 mL 0.5 M NaOAc/HOAc buffer solution (pH 4.7). The mixture was stirred for a few minutes and Na<sub>9</sub>[A- $\alpha$ -PW<sub>9</sub>O<sub>34</sub>] 7H<sub>2</sub>O (0.72 g, 0.28 mmol) was then added all at once. After stirring at room temperature for 1 hr, H<sub>4</sub>L6 (0.10 g, 0.41 mmol) was added to the brown mixture. Stirring was continued for another 2 hr before 1 mL of 1.0 M RbCl solution was added. The solution was filtered to remove any insol-



uble material. Slow evaporation of the solution produced dark brown rhombic crystals after approximately a week (yield 0.15 g, 17% based on W). Elemental analysis, calcd.: H, 1.1%; C, 1.7%; Na, 1.4%; P, 2.5%; Mn, 4.4%; Rb, 9.9%; W, 52.6%; found: H, 2.0%; C, 1.9%; Na, 1.4%; P, 2.2%; Mn, 4.1%; Rb, 10.5%; W, 50.5%; IR (2% KBr pellet, 2000–400 cm<sup>-1</sup>): 1625(vs), 1550(br), 1460(br), 1407(br), 1257(br), 1100(m), 1065(s), 1038(w), 948(vs), 801(br), 735(br), 675(br), 515(br), 421(w).

#### **2a:** $(Me_2NH_2)_{20}Na_2[(B-PW_9O_{34})_2(A-PW_{10}O_{37})_2Mn^{III}_{10}Mn^{IV}_2O_6(OH)_2(O_2CMe)_2(L5)_2]$ 30H<sub>2</sub>O, m.w. 12254.03

A sample of  $Mn(O_2CMe)_3 2H_2O (0.34 \text{ g}, 1.20 \text{ mmol})$  was suspended in a 20 mL 0.5 M NaOAc/HOAc buffer solution (pH 4.7). The mixture was stirred for a few minutes and Na<sub>9</sub>[A- $\alpha$ -PW<sub>9</sub>O<sub>34</sub>] 7H<sub>2</sub>O (0.72 g, 0.28 mmol) was then added all at once. After stirring at room temperature for 1 hr, H<sub>4</sub>L5 (0.05 g, 0.22 mmol) was added to the brown mixture. Stirring was continued for another 2 hr and filtered. Dimethylamine hydrochloride (0.50 g) was added to the resulting filtrate, and



slow evaporation of the solution produced dark brown rhombic crystals after approximately a week (yield 0.15 g, 18.5% based on W). Elemental analysis, calcd.: H, 2.0%; C, 5.3%; N, 2.3%; Na, 0.4%; P, 2.0%; Mn, 5.4%; W, 57.0%; found: H, 2.4%; C, 5.5%; N, 2.3%; Na, 0.5%; P, 2.4%; Mn, 6.0 %; W, 53.8%. IR (2% KBr pellet, 2000–400 cm<sup>-1</sup>): 1591(br), 1550(br), 1465(s), 1440(sh), 1407(br), 1348(br), 1250(br), 1232(br), 1063(br), 1019(w), 960(vs), 855(br), 784(br), 703(w), 678(sh), 602(br), 564(br), 504(br), 453(br), 433(w), 417(w), 405(w).

A sample of  $Mn(O_2CMe)_3 2H_2O (0.34 \text{ g}, 1.20 \text{ mmol})$  was suspended in a 20 mL 0.5 M NaOAc/HOAc buffer solution (pH 4.7). The mixture was stirred for a few minutes and Na<sub>9</sub>[A- $\alpha$ -PW<sub>9</sub>O<sub>34</sub>] 7H<sub>2</sub>O (0.72 g, 0.28 mmol) was then added all at once. After stirring at room temperature for 1 hr, H<sub>4</sub>L4 (0.04 g, 0.20 mmol) was added to the brown mixture. Stirring was continued for another 2 hr and filtered. Dimethylamine hydrochloride (0.50 g) was added to the resulting filtrate, and slow



evaporation of the solution produced dark brown prismatic crystals after approximately a week (yield 0.25 g, 31% based on W). Elemental analysis, calcd.: H, 1.6%; C, 4.0%; N, 1.6%; Na, 1.5%; P, 2.1%; Mn, 5.5%; W, 58.1%; found: calcd.: H, 1.8%; C, 4.5%; N, 1.4%; Na, 1.4 %; P, 2.5%; Mn, 6.0%; W, 56.7%. IR (2% KBr pellet, 2000–400 cm<sup>-1</sup>): 1615(sh), 1582(br), 1465(s), 1440(sh), 1407(br), 1348(br), 1250(br), 1232(br), 1078(br), 1068(br), 1019(w), 958(vs), 855(br), 781(br), 707(w), 604(w), 506(s), 433(w).

#### (2) Instruments and Physical Measurements

IR spectra (KBr pellets) were collected on a Thermo Nicolet Avatar 360 FTIR spectrophotometer. Atmosphere compensation (CO<sub>2</sub> and H<sub>2</sub>O) and baseline corrections were carried out after spectrum collection. <sup>1</sup>H and <sup>31</sup>P NMR spectra (room temperature) were collected on a Bruker Avance III 400MHz NMR instrument. Elemental analyses were performed on a Vario EL III analyzer (for C, H, N) and Perkin-Elmer ICP–OES (for Na, Rb, P, Mn, and W). Thermal gravimetric analyses were measured with a TA Instruments SDT-Q600 thermal analysis system under N<sub>2</sub> flow with 10 °C/min heating. Magnetic measurements were made on polycrystalline samples of **1a**, **2a**, and **3a** using a SQUID magnetometer (PPMS-9T, Quantum Design). Corrections for the capsules and both diamagnetic and temperature-independent paramagnetic contributions were applied to the susceptibility data. All quantum chemical calculations were carried out using Gaussian 09.<sup>3</sup>

Single-crystal X-ray diffraction: suitable crystals were coated with Paratone N oil, suspended on a small fiber loop, and placed in a cooled nitrogen stream at 173(2) K on a Bruker D8 APEX II CCD diffractometer with Mo radiation (for **2a** and **3a**), or a Bruker D8 Quest X-ray diffractometer equipped with an Incoatec Microfocus Mo Source (I $\mu$ S 3.0) and a PHOTON II CPAD detector (for **1a** due to the weak diffracting powder of the crystal).



Fig. S1. Comparison of the IR spectra of 1a and its precursors, A-{PW<sub>9</sub>} and H<sub>4</sub>L6.



Fig. S2. Comparison of the IR spectra of 2a and H<sub>4</sub>L5.



Fig. S3. Comparison of the IR spectra of 3a and H<sub>4</sub>L4.



Fig. S4. Thermogravimetric analysis trace of 1a. The weight loss of ~6.5% (30–180 °C) is associated with the loss of c.a. 92 water molecules, the loss of ~3.8% (180–600 °C) is due to organic content degradation and the loss of ~3.7% (600–1000 °C) is due to the decomposition of inorganic metal-oxide frameworks of 1a.



Fig. S5. Thermogravimetric analysis trace of 2a. The weight loss of ~4.5% (30–180 °C) is associated with the loss of c.a. 30 water molecules, the loss of ~11.0% (180–600 °C) is due to organic content degradation (including diphosphonates and organic counterions) and the loss of ~6.2% (600–1000 °C) is due to the decomposition of inorganic metal-oxide frameworks of 2a.



Fig. S6. Thermogravimetric analysis trace of 3a. The weight loss of ~3.9% (30–180 °C) is associated with the loss of c.a. 26 water molecules, the loss of ~10.7% (180–600 °C) is due to organic content degradation (including diphosphonates and organic counterions) and the loss of ~5.8% (600–1000 °C) is due to the decomposition of inorganic metal-oxide frameworks of 3a.

**NMR:** Because the **L***n* linkers are in close proximity to the paramagnetic Mn centers, their <sup>1</sup>H NMR signals show significant line broadening. The methyl resonance from the acetate ligands of **2a** and **3a**, however, are rather sharp, indicating that these bridging acetate groups are very labile. The <sup>31</sup>P signals (the **L***n* diphosphonates and phosphates from POM ligands) are all too broadened to be observed.



**Fig. S7**. <sup>1</sup>H NMR spectra of H<sub>4</sub>L6 (in D<sub>2</sub>O) and **1a** (in D<sub>2</sub>O). The signal at 1.82 ppm matches well with the acetate proton peaks for **2a** and **3a**, and thus it is believed to come from the acetate impurity because the crystals were isolated from a 0.5 M HOAc/NaOAc buffer solution.



**Fig. S8**. <sup>1</sup>H NMR spectra of H<sub>4</sub>L5 (in D<sub>2</sub>O) and **2a** (in D<sub>2</sub>O). The methylene proton signals of **2a** are not resolved because they are so broadened and likely overlapped by that of DMA counter ions.



**Fig. S9**. <sup>1</sup>H NMR spectra of  $H_4L4$  (in  $D_2O$ ) and **3a** (in  $D_2O$ ).

#### (4) Single-Crystal X-ray Structure Determination

A sphere of data was measured using a series of combinations of  $\phi$  and  $\omega$  scans with 20s (**2a** and **3a**) or 30s (**1a**) frame exposures and 0.5 ° frame widths. Data collection, indexing, frame integration, and final cell refinements were all handled using APEX II (**2a** and **3a**) or APEX III (**1a**) software. The SADABS program was used to carry out absorption corrections. The structure was solved using Direct Methods and difference Fourier techniques (SHELXTL, V6.14).

All metal atoms (Mn and W) on the polyoxometalate frameworks and the heavy Rb counter ions were refined anisotropically. Lighter atoms such as Na, P, and O were in general refined isotropically (only anisotropically when quality of the data permitted). Some of the cationic counterions (Rb<sup>+</sup>, Na<sup>+</sup>, and DMA<sup>+</sup>) and the lattice water molecules could not be located due to disorder. Therefore, thermogravimetric and elemental analyses were used to determine the number of water molecules and countercations, instead.

For **1a**, its outer Keggin units suffer from different degree of  $\alpha$ -/ $\beta$ - rotational disorder and they are modelled accordingly. For **2a**, a different type of rational disorder involving entire Keggin units are seen, and they are modelled and refined as such. As a result of the disorders, the largest electron density residuals after the final refinement cycles for **1a** and **2a** are predominantly around the disordered heavy W atoms.

CCDC 1814303–1814305 contain the supplementary crystal data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/data\_request/cif.



Fig. S10. The construction of 1 from organic L6 and inorganic POM building blocks.

Identification code	C61229	
Empirical formula	C36 H280 Mn20 Na15 C	0416 P20 Rb29 W72
Formula weight	25149.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 26.7196(14) Å	α= 63.5248(15)°.
	b = 33.0481(17) Å	β= 70.9142(15) °.
	c = 35.0313(19) Å	γ = 85.3875(15) °.
Volume	26089(2) Å <sup>3</sup>	
Z	2	
Density (calculated)	3.201 Mg/m <sup>3</sup>	
Absorption coefficient	19.123 mm <sup>-1</sup>	
F(000)	22380	
Crystal size	0.200 x 0.100 x 0.100 m	m <sup>3</sup>
Theta range for data collection	2.163 to 28.298 °.	
Index ranges	-35<=h<=35, -44<=k<=4	44, -46<=l<=46
Reflections collected	401151	
Independent reflections	128961 [R(int) = 0.1998	]
Completeness to theta = 25.242 $^{\circ}$	99.9 %	
Absorption correction	Semi-empirical from equ	ivalents
Refinement method	Full-matrix-block least-s	quares on F <sup>2</sup>
Data / restraints / parameters	128961 / 235 / 3157	
Goodness-of-fit on F <sup>2</sup>	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.1065, wR2 = 0.2	110
R indices (all data)	R1 = 0.2514, $wR2 = 0.2514$	832
Largest diff. peak and hole	6.637 and -3.801 e.Å <sup>-3</sup>	

 Table S1. Crystal data and structure refinement for 1a (CCDC deposit number: 1814305).



Fig. S11. The construction of 2 and 3 from the POM-based  $Mn_4$  and  $Mn_2$  magnetic clusters.

Table S2.	Crystal	data and	structure	refinement	for <b>2</b>	a (CCD	C de	posit	number:	181430	4)
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Identification code	0510lzw			
mpirical formula C54 H248 Mn12 N20 Na2 O196 P8 W		96 P8 W38		
Formula weight	12254.03			
Temperature	173(2) K			
Wavelength	0.71073 Å			
Crystal system	Monoclinic			
Space group	C 2/c			
Unit cell dimensions	a = 38.5337(5) Å	<i>α</i> = 90 °.		
	b = 27.5478(4) Å	β= 95.5062(16) °.		
	c = 47.9165(12) Å	$\gamma = 90$ °.		
Volume	50629.5(16) Å <sup>3</sup>			
Z	8			
Density (calculated)	3.215 Mg/m <sup>3</sup>			
Absorption coefficient	17.920 mm <sup>-1</sup>			
F(000)	44272			
Crystal size	0.120 x 0.070 x 0.060 mm <sup>3</sup>			
Theta range for data collection	2.907 to 28.703 °.			
Index ranges	-51<=h<=42, -37<=k<=32, -64	<=l<=60		
Reflections collected	122401			
Independent reflections	56996 [R(int) = 0.0903]			
Completeness to theta = $25.242^{\circ}$	99.8 %			
Absorption correction	Semi-empirical from equivalen	ıts		
Max. and min. transmission	0.8021 and 0.6305			
Refinement method	Full-matrix least-squares on F <sup>2</sup>			
Data / restraints / parameters	56996 / 52 / 1590			
Goodness-of-fit on F <sup>2</sup>	1.124			
Final R indices [I>2sigma(I)]	R1 = 0.1356, wR2 = 0.2412			
R indices (all data)	R1 = 0.2106, wR2 = 0.2769			
Largest diff. peak and hole	5.346 and -4.028 e.Å <sup>-3</sup>			

Table S3.	Crystal data	and structure	refinement fo	or <b>3a</b> (CC	DC depo	osit number:	1814303)
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Identification code 10241zw				
Empirical formula	C40 H188 Mn12 N14 Na8 O192 P8 W38			
Formula weight	12015.29			
Temperature	173(2) K			
Wavelength	0.71073 Å			
Crystal system	Monoclinic			
Space group	P 21/n			
Unit cell dimensions	a = 23.6193(6) Å	α= 90 °.		
	b = 46.4612(7) Å	β=114.241(4) °.		
	c = 24.2477(11) Å	$\gamma = 90$ °.		
Volume	24262.8(15) Å <sup>3</sup>			
Z	4			
Density (calculated)	3.289 Mg/m <sup>3</sup>			
Absorption coefficient	18.701 mm <sup>-1</sup>			
F(000)	21528			
Crystal size	0.180 x 0.120 x 0.030 mm <sup>3</sup>			
Theta range for data collection	2.986 to 29.080 °.			
Index ranges	-29<=h<=29, -61<=k<=62, -32	<=l<=30		
Reflections collected	227661			
Independent reflections	57774 [R(int) = 0.1562]			
Completeness to theta = $25.242^{\circ}$	99.8 %			
Absorption correction	Semi-empirical from equivalents			
Max. and min. transmission	0.8935 and 0.7212			
Refinement method	Full-matrix least-squares on F <sup>2</sup>			
Data / restraints / parameters	57774 / 9 / 1545			
Goodness-of-fit on F <sup>2</sup>	1.195			
Final R indices [I>2sigma(I)]	R1 = 0.0981, wR2 = 0.2123			
R indices (all data)	R1 = 0.2114, wR2 = 0.2673			
Largest diff. peak and hole	4.978 and -2.624 e.Å <sup>-3</sup>			

## (5) Bond Valence Sum (BVS) Calculations:

For determination of the oxidation states of metal centers and the protonation states of oxygen sites, BVS calculations were carried out using the method of I. D. Brown<sup>4</sup>. The  $r_0$  values were taken from the literature for calculations performed on Mn<sup>5</sup>.

aamnaunda	manganese atoms		BVS		assigned
compounds		Mn(II)	Mn(III)	Mn(IV)	oxidation states
	Mn1	3.055	2.795	2.934	III
	Mn2	3.249	2.972	3.120	III
	Mn3	2.982	2.727	2.863	III
	Mn4	3.261	2.983	3.132	III
	Mn5	3.288	3.007	3.157	III
	Mn6	3.349	3.063	3.216	III
	Mn7	3.185	2.913	3.058	III
	Mn8	3.057	2.796	2.936	III
	Mn9	3.314	3.031	3.182	III
1.	Mn10	3.237	2.961	3.109	III
14	Mn11	3.335	3.050	3.203	III
	Mn12	3.427	3.134	3.291	III
	Mn13	2.916	2.667	2.800	III
	Mn14	3.212	2.938	3.085	III
	Mn15	3.451	3.157	3.314	III
	Mn16	3.464	3.168	3.326	III
	Mn17	2.899	2.651	2.783	III
	Mn18	3.023	2.765	2.903	III
	Mn19	3.312	3.030	3.181	III
	Mn20	3.263	2.984	3.133	III
	Mn1	3.290	3.009	3.159	III
	Mn2	3.339	3.054	3.206	III
	Mn3	3.409	3.118	3.274	III
2a	Mn4	4.410	4.034	4.235	IV
	Mn5	3.245	2.968	3.116	III
	Mn6	3.158	2.889	3.033	III
	Mn7	3.462	3.167	3.325	III

Table S4. BVS calculations for Mn sites in 1a, 2a, and 3a.

	Mn8	4.056	3.710	3.895	IV
	Mn9	3.294	3.013	3.163	III
	Mn10	3.327	3.043	3.195	III
	Mn11	3.357	3.071	3.224	III
	Mn12	3.397	3.107	3.262	III
	Mn1	3.359	3.072	3.225	III
	Mn2	3.220	2.945	3.092	III
	Mn3	3.274	2.995	3.144	III
	Mn4	4.116	3.765	3.953	IV
	Mn5	3.157	2.888	3.032	III
30	Mn6	3.143	2.875	3.018	III
54	Mn7	3.388	3.099	3.253	III
	Mn8	4.214	3.855	4.047	IV
	Mn9	3.208	2.934	3.080	III
	Mn10	3.270	2.991	3.140	III
	Mn11	3.213	2.939	3.085	III
	Mn12	3.344	3.059	3.211	III

Table S4. BVS calculations for selected oxygen atoms in 1a, 2a, and 3a.

compounds	selected oxygen atoms	BVS	assigned protona- tion levels
	O35	1.129	ОН
	O36	0.240	$H_2O$
	O77	1.154	ОН
	O78	0.275	H <sub>2</sub> O
	O117	1.192	ОН
	O118	0.339	H <sub>2</sub> O
10	O159	1.138	ОН
18	O160	0.295	$H_2O$
	O199	1.187	ОН
	O200	0.304	$H_2O$
	O240	1.122	ОН
	O243	0.299	H <sub>2</sub> O
	O279	1.216	ОН
	O280	0.329	H <sub>2</sub> O

	O320	1.210	ОН
	O321	0.281	H <sub>2</sub> O
).	O123	1.176	ОН
2a	O163	1.149	ОН
30	O123	1.228	ОН
Ja	O162	1.203	ОН

## (6) Magnetic Studies



The 300–40 K M(T) data of **2a** and **3a** were well fit to the theoretical  $\chi_M T$  vs T expression for two Mn<sub>4</sub> and two Mn<sub>2</sub> clusters (see Figure 3a, inset, in the manuscript text), assuming no inter-cluster interactions. The Heisenberg exchange Hamiltonian is given by eqn (1):

$$\widehat{H} = -2J_1(\widehat{S}_1\widehat{S}_2 + \widehat{S}_2\widehat{S}_3 + \widehat{S}_1\widehat{S}_3) - 2J_2(\widehat{S}_1\widehat{S}_4 + \widehat{S}_2\widehat{S}_4 + \widehat{S}_3\widehat{S}_4) - 2J_3\widehat{S}_5\widehat{S}_6$$
(1)

where  $J_1$ ,  $J_2$ , and  $J_3$  refer to exchange interactions for Mn<sup>III</sup>–Mn<sup>III</sup> and Mn<sup>III</sup>–Mn<sup>IV</sup> pairs in the Mn<sub>4</sub> clusters and the Mn<sup>III</sup>–Mn<sup>III</sup> pair in the Mn<sub>2</sub> clusters, respectively.



**Fig. S12**. Temperature dependence of  $\chi_M T$  for **1a** at 0.1 T.



Fig. S13. The  $1/\chi_M$  vs T curve (1a) was fit to the Curie-Weiss equation from 300 to 50 K (C = 65.53 emu K mol<sup>-1</sup>,  $\theta = -27.70$  K)



Fig. S14. The *M* vs *H* plot of 1a.



Fig. S15. Comparison of the *M* vs *H* plots of 2a and 3a.

#### (7) Computational Studies

To gain insights into how the distortion of the **L6** chain might alter the outcome of the hybridization, we have performed DFT calculations on the chain-length effect. The geometries of all conformations of the  $P-(CH_2)_6-P$  chain in **L6** have been optimized at the B3LYP/6-31G (2d, 2p) level of density functional theory (DFT)<sup>6</sup> in Gaussian 09 software package.<sup>3</sup> It has been found that the C–C–C–C torsion angles<sup>7</sup> on the alkylene chain in **L6** considerably influence its conformation and hence the stability of molecular

hybrids. A plot of total energy of their stable configurations (**SI** to **SV**) vs the P  $\cdots$  P distance is given by Fig. S16. The calculated results indicate that the energy Eigen value of each conformation is strongly dependent on the number of dihedral angles that are less than 90° in the alkylene chain. The conformation (**SI**) with longest chain length (P  $\cdots$  P distance = 9.50 Å), where all C–C–C–C dihedral angles are nearly 180°, possesses the lowest energy as expected. Conformations **SI** and **SII** are in fact those that are observed in the crystal structure of **1**, and the calculated P  $\cdots$  P distances are very close to those determined from X-ray diffraction. On the other hand, the **SV** conformation (P  $\cdots$  P distance = 5.63 Å) with all three dihedral angles  $\leq$ 90° has the largest energy Eigen value, which is 2.86 kcal/mol higher than the **SI** conformation. The results thus explain why **L6** would not form a similar hybrid to **2** or **3**, as a suppressed P  $\cdots$  P distance to less than 6 Å will lead to an unstable conformation of the **L6** chain.

It is also interesting to note that shortening the  $P \cdots P$  distance of **L6** does not necessarily increase its total energy, and vice versa. For instance, conformation **SII** ( $P \cdots P$  distance, 8.94 Å) is in fact in a higher energy state than **SIII** ( $P \cdots P$  distance, 8.11 Å); lengthening the distance of **SIII** does not induce stability, only to see its energy surge by 1.40 kcal/mol. It is therefore the dihedral angles that dictate the total energy and hence stability of the hybrid complexes.



Fig. S16. DFT calculation results on the stable conformations of L6. The total energy of each conformation is plotted against the P…P distance. The number of C–C–C–C torsion angles that are  $\leq 90^{\circ}$  in each conformation: SI (0), SII (2), SIII (1), SIV(2), SV(3).



Fig. S17. Simulated and experimental powder X-ray diffraction patterns for compound 2a.



Fig. S18. Simulated and experimental powder X-ray diffraction patterns for compound 3a.

### (9) References

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