Supplementary Information

for

Cyclomatrix Polyphosphazenes by the Opening of Sulfur-containing Spiro Rings: Monomer Synthesis, Polymerization, and Optical Properties.

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The details of single crystal x-ray crystallography of **1**, **2**, **3**, and **4** are provided in the following Tables. The molecular structure of **1**, **2**, and **3** determined by single crystal x-ray crystallography are shown in the following Figures. Disordered atoms were found in the difference Fourier maps of **2** and **4**. The occupancy for each disordered atom was refined initially, and was fixed at the final refinement run. The C7 atom in **2** showed large thermal motion due to disorder. The two hydrogen atoms on C4 in **4** were seen in the difference Fourier map and were placed at the very end of the refinement.

Table 1S. Crystallographic data collection and structure refinement parameters for $N_3P_3Cl_4(NHCH_2CH_2S)$.

Empirical formula	$C_2H_5Cl_4N_4P_3S$
Formula weight	351.87
Temperature / K	298(2)
Crystal system	Monoclinic
Space group	P2(1)/n
a / Å	14.2552(13)
b / Å	6.0436(6)
c / Å	15.5469(14)
α / deg	90
β / deg	113.376(2)
γ / deg	90
Volume / $Å^3$	1229.5(2)
Z	4
Density (calculated) / g cm^{-3}	1.901
Absorption coefficient / mm^{-1}	1.490
F(000)	696
Crystal size / mm^3	0.19 × 0.09 × 0.07
Theta range for data collection / deg	From 1.64 to 28.25
Index ranges	$-18 \le h \le 18$, $-8 \le k \le 8$, $-20 \le l \le 19$
Reflections collected	10107
Independent reflections	3006
R_{int}	0.0251
Completeness to theta = 28.25°	99.0%
Absorption correction	Empirical
Ratio of min. and max. transmission	0.6839
Refinement method	Full-matrix least-square on F_2
Data	3006
Restraints	0
Parameters	127
Goodness-of-fit on F^2	1.073
Final R indices	R1 = 0.0681, wR2 = 0.1899
R indices (all data)	R1 = 0.0842, wR2 = 0.2031
Largest diff. peak / e^- $Å^{-3}$	1.158
Largest diff. hole / e^- $Å^{-3}$	–0.806

Table 2S. Crystallographic data collection and structure refinement parameters for *trans*-$N_3P_3Cl_2(NHCH_2CH_2S)_2$.

Empirical formula	$C_4H_{10}Cl_2N_5P_3S_2$
Formula weight	356.10
Temperature / K	93(2)
Crystal system	Monoclinic
Space group	P2(1)
a / Å	9.850(2)
b / Å	11.225(2)
c / Å	12.684(3)
α / deg	90
β / deg	100.897(3)
γ / deg	90
Volume / $Å^3$	1377.2 (5)
Z	4
Density (calculated) / g cm^{-3}	1.717
Absorption coefficient / mm^{-1}	1.104
F(000)	720
Crystal size / mm^3	0.28 × 0.24 × 0.19
Theta range for data collection / deg	From 1.77 to 28.33
Index ranges	$-12 \le h \le 11$, $-18 \le k \le 13$, $-28 \le l \le 26$
Reflections collected	13157
Independent reflections	6658
R_{int}	0.0197
Completeness to theta = 28.32°	99.7%
Absorption correction	Empirical
Ratio of min. and max. transmission	0.7016
Refinement method	Full-matrix least-square on F_2
Data	6658
Restraints	1
Parameters	289
Goodness-of-fit on F^2	1.031
Final R indices	R1 = 0.0294, wR2 = 0.753
R indices (all data)	R1 = 0.0298, wR2 = 0.756
Largest diff. peak / e^- $Å^{-3}$	0.946
Largest diff. hole / e^- $Å^{-3}$	–0.750

Table 3S. Crystallographic data collection and structure refinement parameters for *cis*-$N_3P_3Cl_2(NHCH_2CH_2S)_2$.

Empirical formula	$C_8H_{20}Cl_4N_{10}P_6S_4$
Formula weight	712.20
Temperature / K	273(2)
Crystal system	Monoclinic
Space group	P2(1)/n
a / Å	9.1908(6)
b / Å	13.5389(9)
c / Å	21.8660(15)
α / deg	90
β / deg	94.6750(10)
γ / deg	90
Volume / $Å^3$	2711.8 (3)
Z	4
Density (calculated) / g cm^{-3}	1.744
Absorption coefficient / mm^{-1}	1.121
F(000)	1440
Crystal size / mm^3	0.18 × 0.15 × 0.14
Theta range for data collection / deg	From 1.77 to 28.33
Index ranges	$-12 \le h \le 11$, $-18 \le k \le 13$, $-28 \le l \le 26$
Reflections collected	17485
Independent reflections	6672
R_{int}	0.0207
Completeness to theta = 28.33°	98.5%
Absorption correction	Empirical
Ratio of min. and max. transmission	0.8361
Refinement method	Full-matrix least-square on F_2
Data	6672
Restraints	0
Parameters	289
Goodness-of-fit on F^2	1.032
Final R indices	R1 = 0.0380, wR2 = 0.0971
R indices (all data)	R1 = 0.0478, wR2 = 0.1026
Largest diff. peak / e^- $Å^{-3}$	0.620
Largest diff. hole / e^- $Å^{-3}$	–0.520

Table 4S. Crystallographic data collection and structure refinement parameters for *trans*-$N_3P_3(NHCH_2CH_2S)_3$.

Empirical formula	$C_6H_{15}N_6P_3S_3$
Formula weight	360.31
Temperature / K	133(2)
Crystal system	Orthorhombic
Space group	Pbcn
a / Å	11.316(2)
b / Å	16.802(4)
c / Å	15.148(3)
α / deg	90
β / deg	90
γ / deg	90
Volume / $Å^3$	2880.1(10)
Z	8
Density (calculated) / g cm^{-3}	1.653
Absorption coefficient / mm^{-1}	0.839
F(000)	1472
Crystal size / mm^3	0.20 × 0.15 × 0.13
Theta range for data collection / deg	From 2.17 to 28.30
Index ranges	$-15 \le h \le 15$, $-22 \le k \le 22$, $-19 \le l \le 20$
Reflections collected	25831
Independent reflections	3584
R_{int}	0.0350
Completeness to theta = 28.30°	99.9%
Absorption correction	Empirical
Ratio of min. and max. transmission	0.8503
Refinement method	Full-matrix least-square on F_2
Data	3584
Restraints	0
Parameters	212
Goodness-of-fit on F^2	1.268
Final R indices	R1 = 0.0538, wR2 = 0.1287
R indices (all data)	R1 = 0.0584, wR2 = 0.1306
Largest diff. peak / $e^- Å^{-3}$	0.545
Largest diff. hole / $e^- Å^{-3}$	–0.690

Figure 1S. Molecular structure of **1** determined by single crystal X-ray crystallography.

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Figure 2S. Molecular structure of **2** determined by single crystal X-ray crystallography.

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Figure 3S. Molecular structure of **3** determined by single crystal X-ray crystallography.

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