Electronic Supplementary Information

N-salicylidene aniline derivatives based on the *N'*-thiophosphorylated thiourea scaffold

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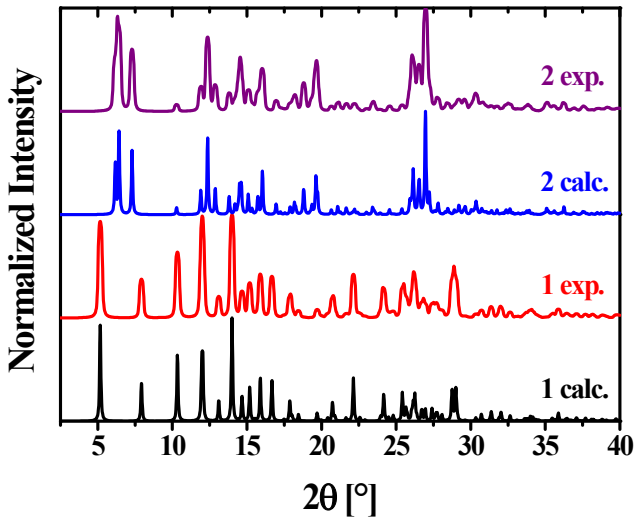

Fig. S1 Calculated and experimental X-ray powder diffraction patterns of **1** and **2**.

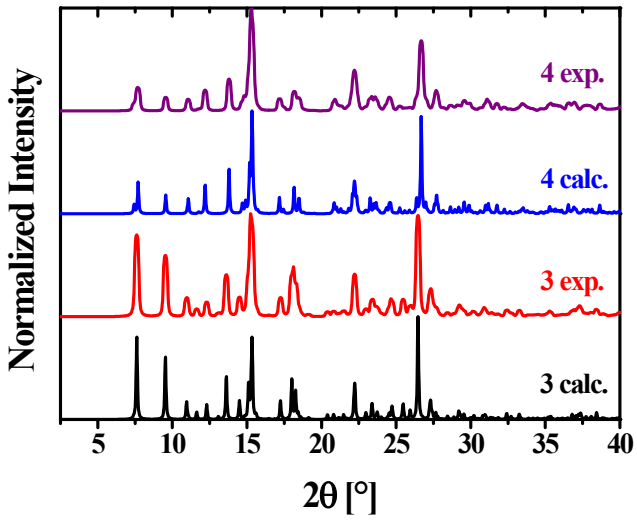

Fig. S2 Calculated and experimental X-ray powder diffraction patterns of **3** and **4**.

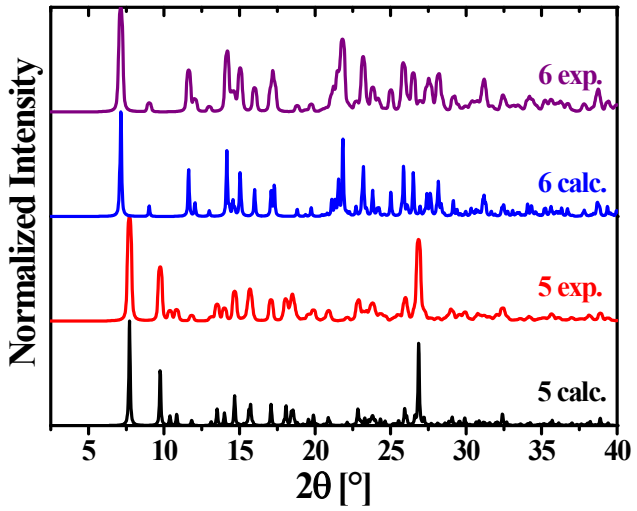

Fig. S3 Calculated and experimental X-ray powder diffraction patterns of **5** and **6**.

Table S1 Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths					
S(1)–P(1)	1.917(4)	P(1)–N(1)	1.674(7)	N(2)–C(1)	1.339(11)
S(2)–C(1)	1.679(10)	N(1)–C(1)	1.369(11)	N(2)–C(11)	1.426(11)
Bond angles					
S(1)–P(1)–N(1)	117.2(3)	C(1)–N(2)–C(11)	131.7(8)	S(2)–C(1)–N(2)	120.9(7)
P(1)–N(1)–C(1)	126.2(6)	S(2)–C(1)–N(1)	122.8(7)	N(1)–C(1)–N(2)	116.2(8)
Torsion angles					
S(1)–P(1)–N(1)–C(1)	–61.0(9)	N(2)–C(1)–N(1)–P(1)	173.1(7)	N(1)–C(1)–N(2)–C(11)	–3.1(16)
S(2)–C(1)–N(1)–P(1)	–5.8(13)	S(2)–C(1)–N(2)–C(11)	175.8(8)		

Table S2 Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths					
S(1)–P(1)	1.9276(11)	N(1)–C(1)	1.360(4)	N(3)–C(8)	1.296(4)
S(2)–C(1)	1.675(3)	N(2)–C(1)	1.366(4)	O(3)–C(22)	1.346(4)
P(1)–N(1)	1.678(3)	N(2)–C(11)	1.407(4)	C(8)–C(21)	1.452(4)
Bond angles					
S(1)–P(1)–N(1)	119.03(9)	C(1)–N(2)–C(11)	130.6(3)	S(2)–C(1)–N(2)	119.6(2)
P(1)–N(1)–C(1)	126.5(2)	S(2)–C(1)–N(1)	124.4(2)	N(1)–C(1)–N(2)	116.0(2)
Torsion angles					
S(1)–P(1)–N(1)–C(1)	–67.4(2)	S(2)–C(1)–N(2)–C(11)	–171.2(2)	C(14)–C(13)–N(3)–C(8)	19.9(4)
S(2)–C(1)–N(1)–P(1)	6.5(4)	N(1)–C(1)–N(2)–C(11)	8.4(4)	N(3)–C(8)–C(21)–C(22)	–0.8(4)
N(2)–C(1)–N(1)–P(1)	–173.07(18)	N(12)–C(13)–N(3)–C(8)	–162.7(3)	N(3)–C(8)–C(21)–C(26)	179.2(3)

Table S3 Selected bond lengths (Å) and bond angles (°) for **3**

Bond lengths					
S(1)–P(1)	1.9259(10)	N(1)–C(1)	1.357(3)	N(3)–C(8)	1.277(3)
S(2)–C(1)	1.672(3)	N(2)–C(1)	1.358(3)	O(3)–C(22)	1.347(4)
P(1)–N(1)	1.685(2)	N(2)–C(11)	1.401(3)	C(8)–C(21)	1.457(4)
Bond angles					
S(1)–P(1)–N(1)	107.08(8)	C(1)–N(2)–C(11)	131.7(2)	S(2)–C(1)–N(2)	119.74(19)
P(1)–N(1)–C(1)	129.76(17)	S(2)–C(1)–N(1)	123.60(18)	N(1)–C(1)–N(2)	116.7(2)
Torsion angles					
S(1)–P(1)–N(1)–C(1)	178.1(2)	S(2)–C(1)–N(2)–C(11)	–179.7(2)	C(14)–C(13)–N(3)–C(8)	–172.1(3)
S(2)–C(1)–N(1)–P(1)	4.9(4)	N(1)–C(1)–N(2)–C(11)	–0.7(4)	N(3)–C(8)–C(21)–C(22)	–1.2(4)
N(2)–C(1)–N(1)–P(1)	–174.2(2)	N(12)–C(13)–N(3)–C(8)	9.0(4)	N(3)–C(8)–C(21)–C(26)	178.0(3)

Table S4 Selected bond lengths (Å) and bond angles (°) for **4**

Bond lengths					
S(1)–P(1)	1.9273(11)	N(1)–C(1)	1.355(4)	N(3)–C(8)	1.292(4)
S(2)–C(1)	1.674(3)	N(2)–C(1)	1.361(3)	O(3)–C(22)	1.337(4)
P(1)–N(1)	1.691(3)	N(2)–C(11)	1.398(3)	C(8)–C(21)	1.450(4)
Bond angles					
S(1)–P(1)–N(1)	107.02(9)	C(1)–N(2)–C(11)	131.2(2)	S(2)–C(1)–N(2)	119.3(2)
P(1)–N(1)–C(1)	129.47(19)	S(2)–C(1)–N(1)	123.81(19)	N(1)–C(1)–N(2)	116.9(2)
Torsion angles					
S(1)–P(1)–N(1)–C(1)	–179.8(3)	S(2)–C(1)–N(2)–C(11)	179.6(3)	C(14)–C(13)–N(3)–C(8)	173.8(3)
S(2)–C(1)–N(1)–P(1)	–1.8(4)	N(1)–C(1)–N(2)–C(11)	0.4(5)	N(3)–C(8)–C(21)–C(22)	0.9(5)
N(2)–C(1)–N(1)–P(1)	177.4(2)	N(12)–C(13)–N(3)–C(8)	–6.8(5)	N(3)–C(8)–C(21)–C(26)	–178.9(3)

Table S5 Selected bond lengths (Å) and bond angles (°) for **5**

Bond lengths					
S(1)–P(1)	1.9240(10)	N(1)–C(1)	1.355(3)	N(3)–C(8)	1.282(3)
S(2)–C(1)	1.663(3)	N(2)–C(1)	1.363(3)	O(3)–C(22)	1.341(3)
P(1)–N(1)	1.682(2)	N(2)–C(11)	1.394(3)	C(8)–C(21)	1.447(4)
Bond angles					
S(1)–P(1)–N(1)	106.83(9)	C(1)–N(2)–C(11)	131.6(2)	S(2)–C(1)–N(2)	119.87(19)
P(1)–N(1)–C(1)	129.63(18)	S(2)–C(1)–N(1)	123.62(19)	N(1)–C(1)–N(2)	116.5(2)
Torsion angles					
S(1)–P(1)–N(1)–C(1)	–177.1(2)	S(2)–C(1)–N(2)–C(11)	–176.8(2)	C(14)–C(13)–N(3)–C(8)	–172.6(2)
S(2)–C(1)–N(1)–P(1)	0.5(4)	N(1)–C(1)–N(2)–C(11)	2.6(4)	N(3)–C(8)–C(21)–C(22)	-0.2(4)
N(2)–C(1)–N(1)–P(1)	–178.8(2)	N(12)–C(13)–N(3)–C(8)	7.9(4)	N(3)–C(8)–C(21)–C(26)	–177.7(2)

Table S6 Selected bond lengths (Å) and bond angles (°) for **6**

Bond lengths					
S(1)–P(1)	1.922(2)	N(1)–C(1)	1.367(7)	N(3)–C(8)	1.293(6)
S(2)–C(1)	1.657(6)	N(2)–C(1)	1.363(6)	O(3)–C(22)	1.330(6)
P(1)–N(1)	1.683(4)	N(2)–C(11)	1.402(7)	C(8)–C(21)	1.434(7)
Bond angles					
S(1)–P(1)–N(1)	106.82(17)	C(1)–N(2)–C(11)	132.3(5)	S(2)–C(1)–N(2)	120.0(4)
P(1)–N(1)–C(1)	128.6(4)	S(2)–C(1)–N(1)	124.2(4)	N(1)–C(1)–N(2)	115.7(5)
Torsion angles					
S(1)–P(1)–N(1)–C(1)	–179.3(5)	S(2)–C(1)–N(2)–C(11)	–177.2(5)	C(14)–C(13)–N(3)–C(8)	168.9(5)
S(2)–C(1)–N(1)–P(1)	–7.4(8)	N(1)–C(1)–N(2)–C(11)	2.2(9)	N(3)–C(8)–C(21)–C(22)	1.5(8)
N(2)–C(1)–N(1)–P(1)	173.2(4)	N(12)–C(13)–N(3)–C(8)	–10.7(7)	N(3)–C(8)–C(21)–C(26)	178.7(5)

Table S7. Hydrogen bond lengths (Å) and angles (°) for **1–6**

	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
1[a]	N(1)–H(1N)···N(12)	0.86	1.96	2.63(2)	133
	N(2)–H(2N)···S(2)$^{\#1}$	0.86	2.55	3.373(15)	162
2[b]	N(1)–H(1N)···N(12)	0.88	1.95	2.653(3)	136
	N(2)–H(2N)···O(5)$^{\#1}$	0.88	2.03	2.897(4)	170
	O(3)–H(3)···N(3)	0.84	1.88	2.619(4)	147
	O(4)–H(4)···O(5)	0.84	1.91	2.643(4)	145
3[c]	N(1)–H(1N)···N(12)	0.86	1.99	2.705(3)	139
	N(2)–H(2N)···S(2)$^{\#1}$	0.86	2.54	3.387(2)	170
	O(3)–H(3)···N(3)	0.82	1.89	2.614(3)	147
4[d]	N(1)–H(1N)···N(12)	0.88	1.97	2.698(3)	139
	N(2)–H(2N)···S(2)$^{\#1}$	0.88	2.49	3.355(3)	169
	O(3)–H(3)···N(3)	0.84	1.86	2.599(3)	147
5[e]	N(1)–H(1N)···N(12)	0.78(4)	2.04(4)	2.691(3)	141(4)
	N(2)–H(2N)···S(2)$^{\#1}$	0.78(3)	2.57(3)	3.343(2)	170(3)
	O(3)–H(3)···N(3)	0.82(4)	1.84(4)	2.586(3)	152(4)
6[f]	N(1)–H(1N)···N(12)	0.92(5)	1.91(5)	2.700(6)	143(5)
	N(2)–H(2N)···S(2)$^{\#1}$	0.91(4)	2.50(4)	3.397(5)	174(3)
	O(3)–H(3)···N(3)	0.84(6)	1.88(8)	2.564(6)	138(6)
	O(2L)–H(1L)···Br(2)	0.85	2.79	3.643(15)	180

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, 1-z$.
[b] Symmetry transformations used to generate equivalent atoms: #1 1 $-x, 1-y, 1-z$.
[c] Symmetry transformations used to generate equivalent atoms: #1 $-x, 1-y, -z$.
[d] Symmetry transformations used to generate equivalent atoms: #1 $1-x, 1-y, 2-z$.
[e] Symmetry transformations used to generate equivalent atoms: #1 $-x, 1-y, 1-z$.
[f] Symmetry transformations used to generate equivalent atoms: #1 $1-x, -y, 1-z$.

Table S8. π···π bond lengths (Å) and angles (°) for **1–6**[a]

	Cg(*I*)	Cg(*J*)[b]	*d*[Cg(*I*)–Cg(*J*)]	Cg(*I*)_Perp	Cg(*J*)_Perp	*α*	*β*
1[b]	Cg(1)	Cg(1)$^{\#1}$	3.810(6)	3.325(4)	3.313(4)	0	29.2
	Cg(1)	Cg(1)$^{\#1}$	3.6646(16)	3.3435(11)	3.3435(11)	0.03	24.16
2[c]	Cg(2)	Cg(3)$^{\#2}$	4.2119(17)	3.4755(13)	3.4190(9)	4.75	35.73
	Cg(2)	Cg(3)$^{\#3}$	3.9091(17)	3.3726(13)	3.4329(9)	4.75	28.58
3[d]	Cg(1)	Cg(2)$^{\#1}$	3.783(2)	3.4376(12)	3.3635(14)	8.24(15)	27.3
	Cg(2)	Cg(1)$^{\#1}$	3.784(2)	3.3635(14)	3.4376(12)	8.24(15)	24.7
4[e]	Cg(1)	Cg(2)$^{\#1}$	3.643(2)	3.3303(13)	3.2840(14)	6.44(16)	25.7
5[f]	Cg(1)	Cg(2)$^{\#1}$	3.6562(14)	3.3144(9)	3.3676(10)	7.95(11)	22.9
6[g]	Cg(1)	Cg(2)$^{\#1}$	3.857(3)	3.344(2)	3.607(2)	11.4(3)	20.7

[a] Cg(*I*)–Cg(*J*): distance between ring centroids; Cg(*I*)_Perp: perpendicular distance of Cg(*I*) on ring J; Cg(*J*)_Perp: perpendicular distance of Cg(*J*) on ring I; *α*: dihedral angle between planes Cg(*I*) and Cg(*J*); *β*: angle Cg(*I*) → Cg(*J*) vector and normal to plane I. Cg(1): N(12)–C(11)–C(16)–C(15)–C(14)–C(13); Cg(2): C(21)–C(22)–C(23)–C(24)–C(25)–C(26).

[b] Symmetry transformations used to generate equivalent atoms: #1 x, $1/2 - y$, $-1/2 + z$.

[c] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $1 - y$, $2 - z$; #2 $-1 + x$, y, $1 + z$; #3 x, y, $1 + z$.

[d] Symmetry transformations used to generate equivalent atoms: #1 $1 - x$, $1 - y$, $1 - z$.

[e] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $1 - y$, $1 - z$.

[f] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $1 - y$, $2 - z$.

[g] Symmetry transformations used to generate equivalent atoms: #1 $1/2 - x$, $1/2 - y$, $1 - z$.

Table S9. Dihalogen bond lengths (Å) and angles (°) for **3–5**

	X	C–X···X–C	*d*(C–X)	*d*(X···X)	R_{XX}[a]	∠(CXX)
3[b]	Cl	C(25)–Cl(1)···Cl(1)–C(25)	1.741(4)	3.3663(16)	0.9618	154.24(14)
4[c]	Br	C(25)–Br(1)···Br(1)–C(25)	1.897(4)	3.3777(8)	0.9129	152.03(11)
5[d]	Cl	C(25)–Cl(2)···Cl(2)–C(25)	1.739(3)	3.3737(11)	0.9639	154.81(10)

[a] $R_{XX} = d(X\cdots X)/(r_X + r_X)$, where r_X is the van der Waals radii[1] of the halogen atom X (following the definition of Lommerse et al.[2]).

[b] Symmetry transformations used to generate equivalent atoms: $2 - x$, $- y$, $1 - z$.

[c] Symmetry transformations used to generate equivalent atoms: $-1 - x$, $2 - y$, $1 - z$.

[d] Symmetry transformations used to generate equivalent atoms: $2 - x$, $- y$, $2 - z$.

References

1 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

2 J. P. M. Lommerse, A. J. Stone, R. Taylor and F. H. Allen, *J. Am. Chem. Soc.*, 1996, **118**, 3108.