

## Supplementary Information

### Engineering Molecular Crystals with Abnormally Weak Cohesion

Kenneth E. Maly,<sup>†\*</sup> Eric Gagnon<sup>‡</sup> and James D. Wuest<sup>‡</sup>

<sup>†</sup>*Department of Chemistry, Wilfrid Laurier University, Waterloo, Ontario N2L 3C5 Canada*

<sup>‡</sup>*Département de Chimie, Université de Montréal, Montréal, Québec H3C 3J7 Canada*

Contents	Page
I. Experimental Methods	S2
II. <b>Figure S1.</b> Representative thermogravimetric plots showing the rate of sublimation of hexaphenylbenzene <b>1a</b> at different temperatures.	S3
III. <b>Figure S2.</b> Representative thermogravimetric plots showing the rate of sublimation of hexaphenylbenzene <b>1b</b> at different temperatures.	S4
IV. <b>Figure S3.</b> Representative thermogravimetric plots showing the rate of sublimation of hexaphenylbenzene <b>1c</b> at different temperatures.	S5
V. <b>Table S1.</b> Rates of Sublimation of Hexaphenylbenzenes <b>1a-c</b> at Different Temperatures.	S6
VI. <b>Table S2.</b> Vapor Pressure and Rate of Sublimation for Tetraphenylporphyrin <b>2a</b> at Different Temperatures.	S6
VII. <b>Figure S4.</b> Plot of $\ln P$ versus $\ln (dm/dt)$ for tetraphenylporphyrin <b>2a</b> .	S7
VIII. <b>Figure S5.</b> Arrhenius plots of the rates of sublimation versus $1/T$ for hexaphenylbenzenes <b>1a-c</b> .	S8

\*To whom correspondence should be addressed. E-mail: kmaly@wlu.ca

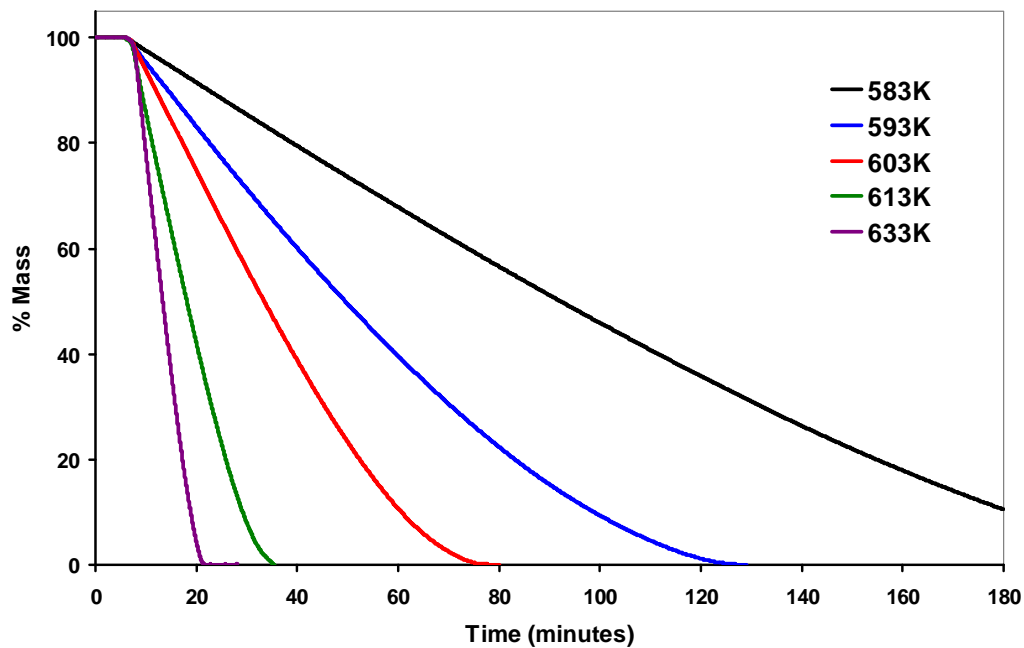
## Experimental Methods

Hexaphenylbenzenes **1a-c** were prepared and crystallized by methods reported previously.<sup>1</sup> Tetraphenylporphyrin **2a** was prepared according to a published procedure and recrystallized from CHCl<sub>3</sub>/CH<sub>3</sub>OH before use.<sup>2</sup> Isothermal thermogravimetry was carried out with a TA Instruments Q50 apparatus, using a dynamic atmosphere of N<sub>2</sub> introduced at a rate of 60 mL/min.

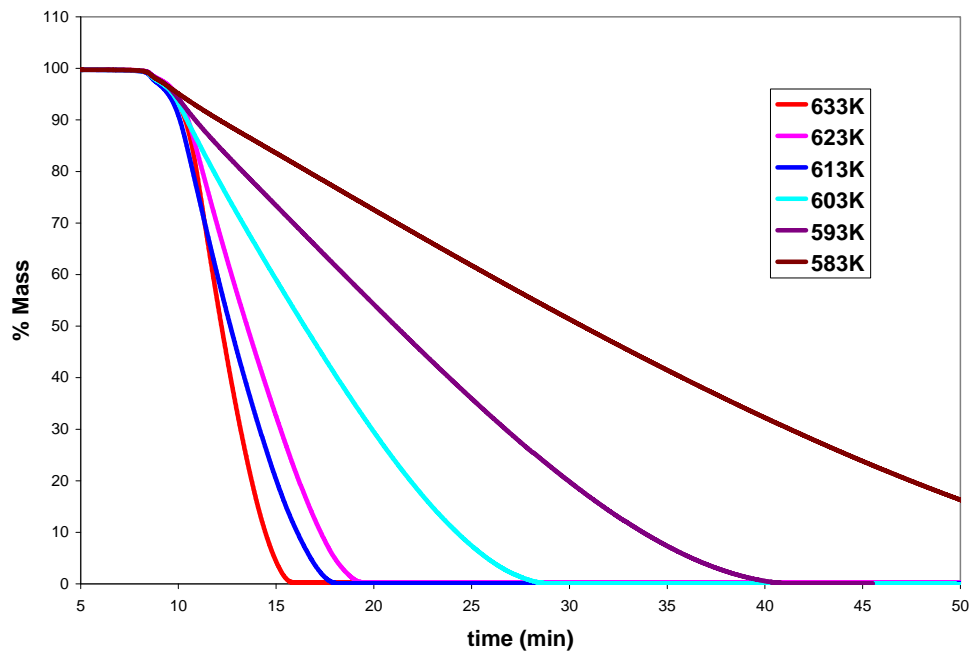
---

<sup>1</sup> J. C. J. Bart, *Acta Crystallogr.* 1968, **B24**, 1277-1287; M. Lutz, A. L. Spek, S. Bonnet, R. J. M. Klein Gebbink and G. van Koten, as communicated in 2006 to the Cambridge Crystallographic Data Centre (CCDC 609800, Refcode: HPHBNZ03) ; E. Gagnon, S. D. Halperin, V. Métivaud, K. E. Maly and J. D. Wuest, *J. Org. Chem.* 2010, **75**, 399-406.

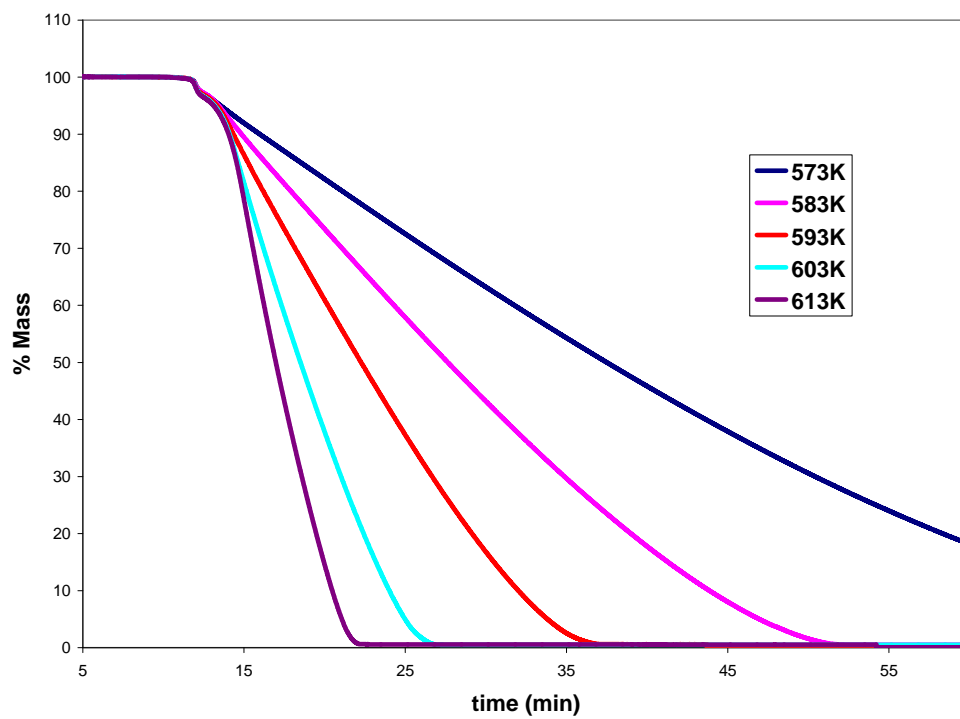
<sup>2</sup> A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.* 1967, **32**, 476.



**Figure S1.** Representative thermogravimetric plots showing the rate of sublimation of hexaphenylbenzene **1a** at different temperatures.



**Figure S2.** Representative thermogravimetric plots showing the rate of sublimation of hexaphenylbenzene **1b** at different temperatures.



**Figure S3.** Representative thermogravimetric plots showing the rate of sublimation of hexaphenylbenzene **1c** at different temperatures.

**Table S1.** Rates of Sublimation of Hexaphenylbenzenes **1a-c** at Different Temperatures.

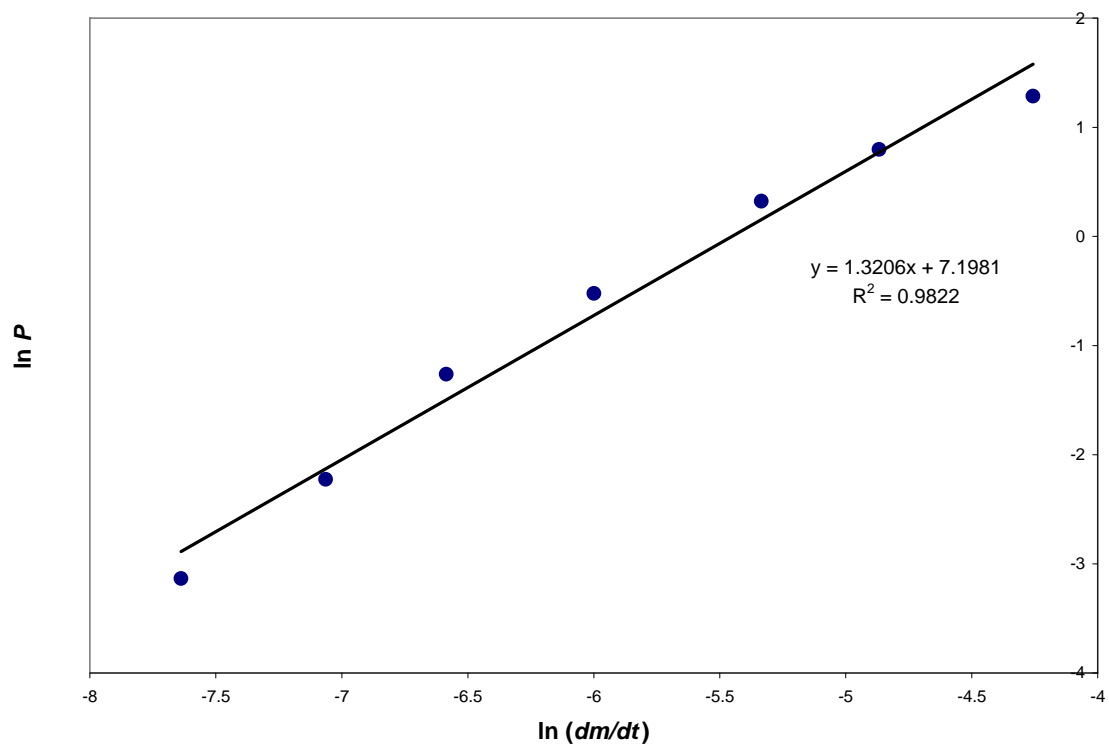
Temperature (K)	Rates of Sublimation (mg/min)		
	<b>1a</b>	<b>1b</b>	<b>1c</b>
573	0.0502	0.1115	0.2698
583	0.0987	0.2184	0.4474
593	0.1603	0.3588	0.7157
603	0.2997	0.5533	1.0083
613	0.4348	0.8293	1.7029
623	0.7373	1.141	2.3236
633 <sup>a</sup>	1.0498	-	-
643 <sup>a</sup>	1.4961	-	-

<sup>a</sup>Rates for compounds **1b-c** were too high at these temperatures to be measured reliably.

**Table S2.** Vapor Pressure and Rate of Sublimation for Tetraphenylporphyrin **2a** at Different Temperatures.

Temperature (K)	Vapor Pressure ( $10^2$ Pa) <sup>a</sup>	$dm/dt$ (mg/min)
593	4.35	0.0004818
603	10.8	0.0008556
613	28.3	0.00138
623	59.3	0.00248
633	138	0.00482
643	222	0.00769
653	361	0.01417

<sup>a</sup>Vapor pressure data obtained from: G. L. Perlovich, O. A. Golubchikov and M. E. Klueva, *J. Porphyrins Phthalocyanines* 2000, **4**, 699-706.



**Figure S4.** Plot of  $\ln P$  versus  $\ln(dm/dt)$  for tetraphenylporphyrin **2a**.

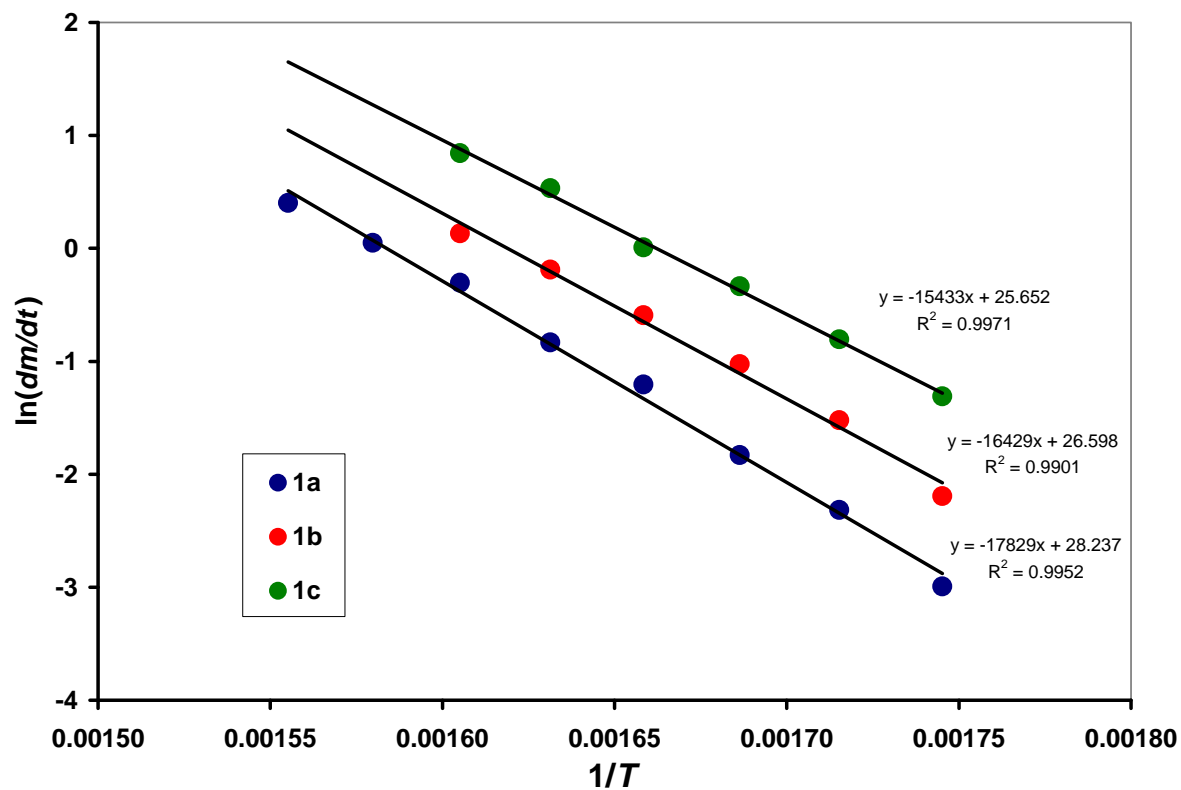


Figure S5. Arrhenius plots of the rates of sublimation versus  $1/T$  for hexaphenylbenzenes **1a-c**.