Supplementary Material for:

Locking high energy 1D chain of dichloromethane molecules containing abnormally short Cl•••Cl contacts of 2.524 Å inside organic crystals

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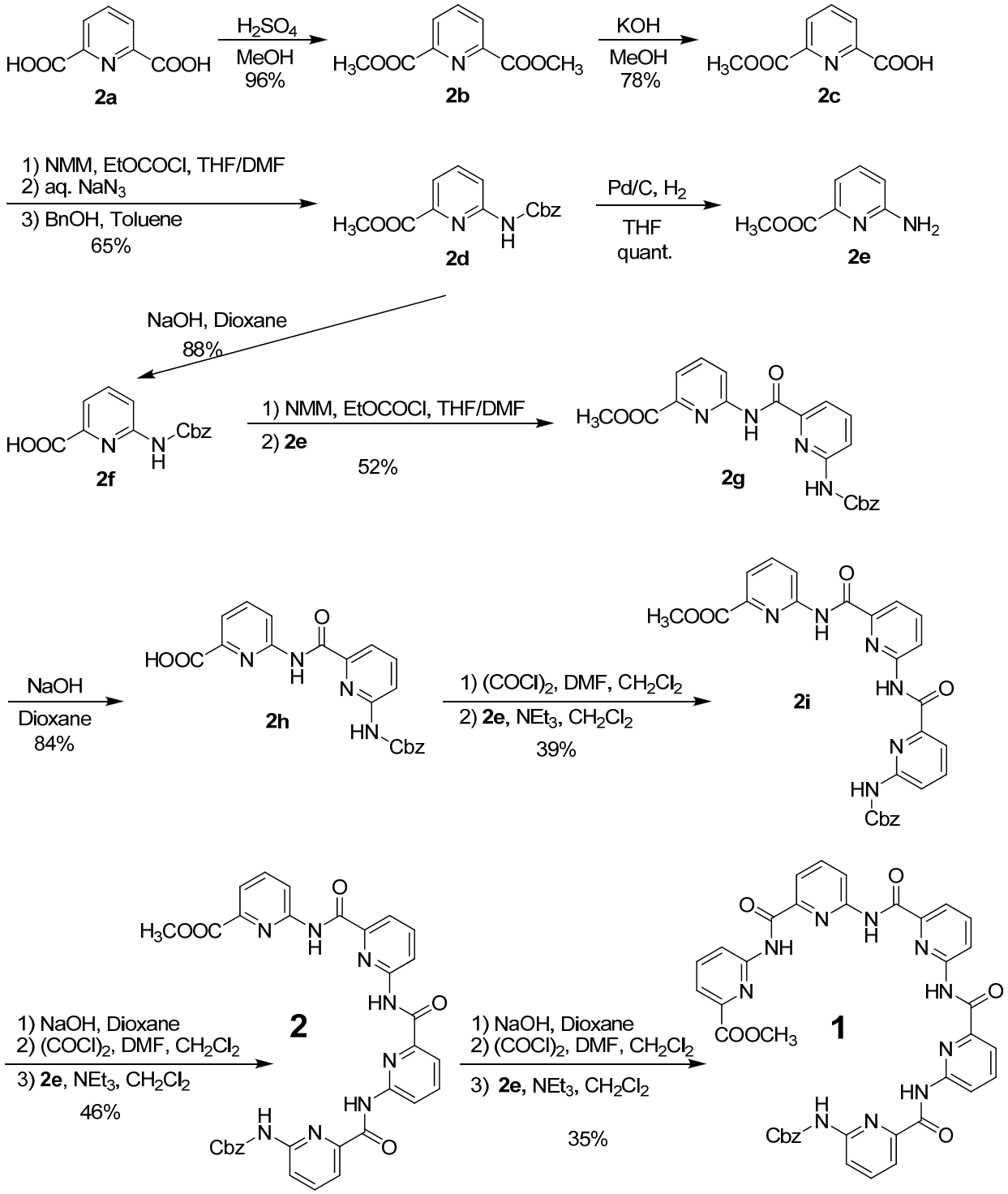
This SI in pdf format contains the following:

1. Scheme S1. Synthetic Route that Affords Pentamer 1

For the synthesis of tetramer **2** from **2a**, see: *Chem. Commun.* **2011**, *47*, 6416.

For the synthesis of pentamer **1** from tetramer **2**, see: *Chem. Sci*. **2012**, *3*, 2042.



2. X-Ray Crystal Data of CH_2Cl_2-containing 1

2a. Crystal data of M1•CH_2Cl_2 containing left-handed helices

CCDC Number	**838392**	
Empirical formula	$C_{40}\ H_{32}\ Cl_2\ N_{10}\ O_8$	
Formula weight	851.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.5103(13) Å	α= 90°.
	b = 13.6620(16) Å	β= 90°.
	c = 25.537(3) Å	γ = 90°.
Volume	3666.9(8) $Å^3$	
Z	4	
Density (calculated)	1.543 Mg/m^3	
Absorption coefficient	0.250 mm^{-1}	
F(000)	1760	
Crystal size	0.60 x 0.20 x 0.18 mm^3	
Theta range for data collection	1.59 to 27.49°.	
Index ranges	-13<=h<=13, -16<=k<=17, -32<=l<=33	
Reflections collected	26068	
Independent reflections	8409 [R(int) = 0.0848]	
Completeness to theta = 27.49°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9611 and 0.9066	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8409 / 35 / 572	
Goodness-of-fit on F^2	1.101	
Final R indices [I>2sigma(I)]	R1 = 0.0866, wR2 = 0.1850	
R indices (all data)	R1 = 0.1167, wR2 = 0.2012	
Absolute structure parameter	0.0(2)	
Largest diff. peak and hole	0.458 and -0.901 e.$Å^{-3}$	

2b. Crystal data of P1•CH_2Cl_2 containing right-handed helices

CCDC Number	**838393**	
Empirical formula	$C_{40}\ H_{32}\ Cl_2\ N_{10}\ O_8$	
Formula weight	851.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.5003(13) Å	α= 90°.
	b = 13.6695(17) Å	β= 90°.
	c = 25.510(3) Å	γ = 90°.
Volume	3661.5(8) $Å^3$	
Z	4	
Density (calculated)	1.545 Mg/m^3	
Absorption coefficient	0.250 mm^{-1}	
F(000)	1760	
Crystal size	0.40 x 0.18 x 0.16 mm^3	
Theta range for data collection	1.60 to 27.50°.	
Index ranges	-13<=h<=13, -17<=k<=16, -33<=l<=30	
Reflections collected	25780	
Independent reflections	8402 [R(int) = 0.0407]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9610 and 0.9065	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8402 / 35 / 572	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1579	
R indices (all data)	R1 = 0.0764, wR2 = 0.1665	
Absolute structure parameter	-0.08(18)	
Largest diff. peak and hole	0.555 and -0.866 $e.Å^{-3}$	

3. Theoretical Computations by dreiding force field[5]

In this paper, the dreiding force field [1] is used to optimize the geometry and calculate the energy of all the structural motifs taken from the respective crystal structures as tabulated in Table 1. The convergence tolerance is $2X10^{-5}$ kcal/mol for the energy, 0.001 kcal/mol/A for the force, 0.001 GPa for the stress and 10^{-5} A for the displacement. The Ewald method is used for calculating the electrostatic and the van der Waals terms. The accuracy is 10^{-5} kcal/mol. The repulsive cutoff is 6 Å for the van der Waals term. For the hydrogen bond term, the summation method is atom based and the truncation method is cubic spline with cutoff distance of 4.5 Å. For the isolated helical pentamer or those made up of up to three pentamers, these molecules are put in a three dimensional cubic box with every lattice length to be 100 Å to avoid the interaction of the molecules with their mirror counterparts. During the optimization the box is fixed and only the molecules are optimized for the isolated case. For the 1D cases, where the molecules repeat periodically in one or two directions, the box vectors are also optimized together with the molecules.

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3. Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.
4. Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, 94, 6081; Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, 89, 2193.
5. Mayo, S. L., Olafson, B. D. & Goddard III, W. A. “Dreiding - A generic force-field for molecular simulations,” *J. Phys. Chem.*, **94**, 8897-909 (1990).