Electronic Supplementary Material (ESI) for ChemComm.

ELECTRONIC SUPPLEMENTARY INFORMATION

Switching of inherent chirality driven by self-assembly

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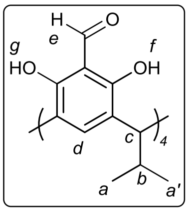
General information

All solvents and chemicals used were purchased from Sigma Aldrich, TCI Europe N. V., Roth, Chem Impex Inc. and Euriso-top, were of reagent grade and were used without further purification. High resolution ESI mass spectra were recorded on a SYNAPT spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 298 K on Bruker 400 MHz instrument with residual solvent signal as internal standard. *J* values are given in Hz. ECD spectra were recorded on Jasco J-715 spectropolarimeter.

Synthesis and analytical data for compounds

1b

Isopropyl resorcin[4]arene was synthesized according to standard literature procedure (0.1 mol of resorcinol was used).[1] (9.85 g, 30 %).
δ_H (400 MHz, $CDCl_3$) 8.99 (8 H, s, OH), 7.45 (4 H, s, C(6)H), 6.15 (4 H, s, C(6)H), 3.72 (4 H, d, *J* 11.3, C(6)CH), 3.11-3.02 (4 H, m, C*H*$(CH_3)_2$), 0.85 (24 H, d, *J* 6.3, CH(C*H*$_3)_2$).
δ_C (100 MHz, $CDCl_3$) 151.4, 125.7, 123.4, 102.5, 41.7, 29.1, 21.6.
HRMS (ESI): *m/z* calc for $C_{40}H_{48}O_8Na$ 679.3247, found 679.3232 (|Δ|=2.2 ppm).
Isopropyl tetraformylresorcin[4]arene was synthesized according to literature procedure (0.8 mmol of resorcin[4]arene was used).[2] (215 mg, 35 %). Acetone used to precipitation resides in the cavity and its complete removal is impossible.



δ_H (400 MHz, $CDCl_3$) 13.13 (4 H, br s, *f*), 10.30 (4 H, s, *e*), 8.34 (4 H, br s, *g*), 7.39 (4 H, br s, *d*), 3.94 (4 H, d, *J* 11.4, *c*), 2.79-2.70 (4 H, m, *b*), 1 (12 H, d, *J* 6.3, *a*), 0.98 (12 H, *J* 6.1, *a'*).
δ_C (100 MHz, $CDCl_3$) 195.6, 156.5, 156.3, 132.4, 123.1, 123.0, 110.8, 40.3, 29.9, 21.34, 21.33.
HRMS (ESI): *m/z* calc for $C_{44}H_{47}O_{12}$ 767.3068, found 767.3054 (|Δ|=1.8 ppm).

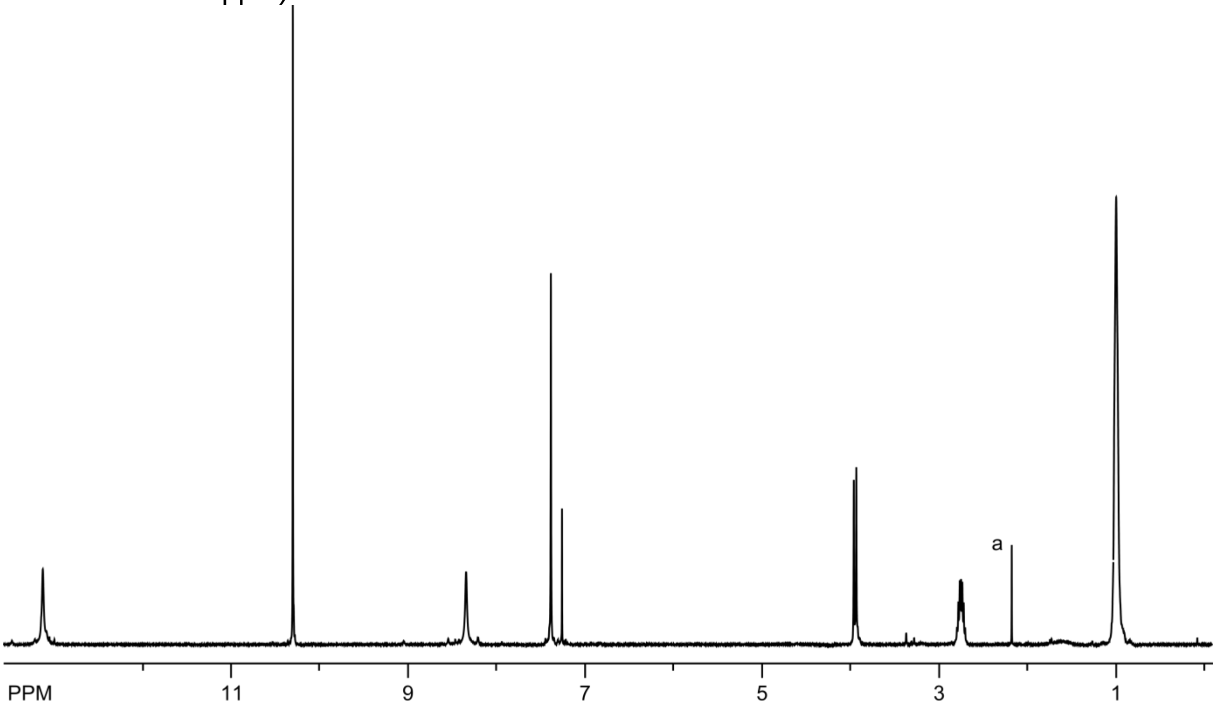


Figure S1. ^{1}H NMR spectrum of **1b** (400 MHz, $CDCl_3$, a - acetone).

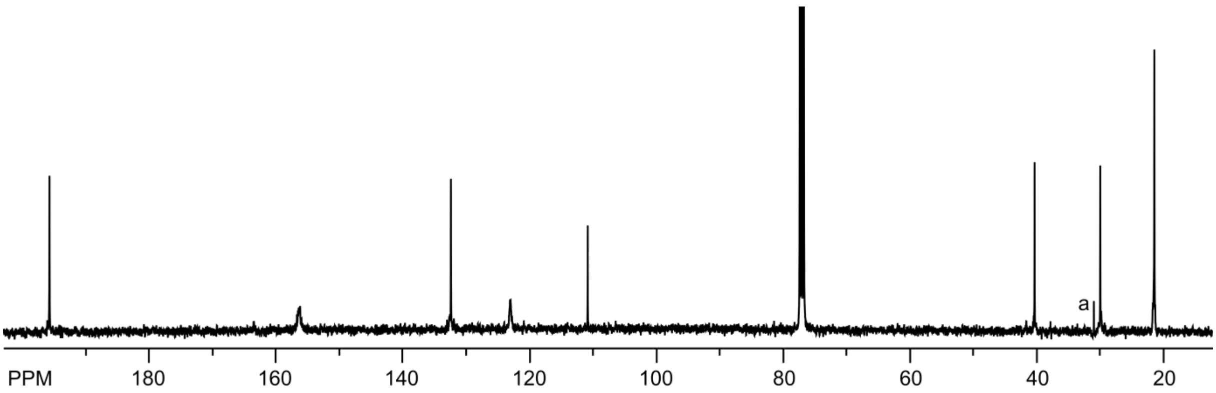
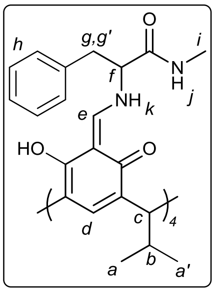


Figure S2. ^{13}C NMR spectrum of **1b** (100 MHz, $CDCl_3$, a - acetone).

(*S*)-2c

Was synthesized according to literature procedure (0.1 mmol of **1b** was used).[3] (132.5 mg, 94 %).



δ_H (400 MHz, $CDCl_3$) 14.85 (4 H, br s, *k*), 9.48 (4 H, br s, OH), 8.72 (4 H, s, *e*), 7.19-7.05 (24 H, m, *d*), 5.81 (4 H, br q, *j*), 4.21 (4 H, d, J_1 4.4, J_2 6.4, *f*), 3.98 (4 H, d, *J* 11.5, *c*), 3.30 (4 H, dd, J_1 6.4, J_2 13.6, *g*), 3.16 (4 H, dd, J_1 4.4, J_2 13.6, *g'*), 2.79 (12 H, d, *J* 4.6, *i*), 2.80-2.70 (4 H, m, *b*), 1.00 (12 H, d, *J* 6.2, *a*), 0.96 (12 H, d, *J* 6.2, *a'*).

δ_C (100 MHz, $CDCl_3$) 170.4, 164.4, 161.0, 154.3, 136.0, 130.2, 129.5, 128.6, 127.0, 125.0, 121.0, 108.0, 72.5, 41.2, 40.5, 29.5, 26.3, 21.57, 21.55.

HRMS (ESI): *m/z* calc for $C_{84}H_{97}N_8O_{12}$ 1409.7226, found 1409.7208 (|Δ|=1.3 ppm).

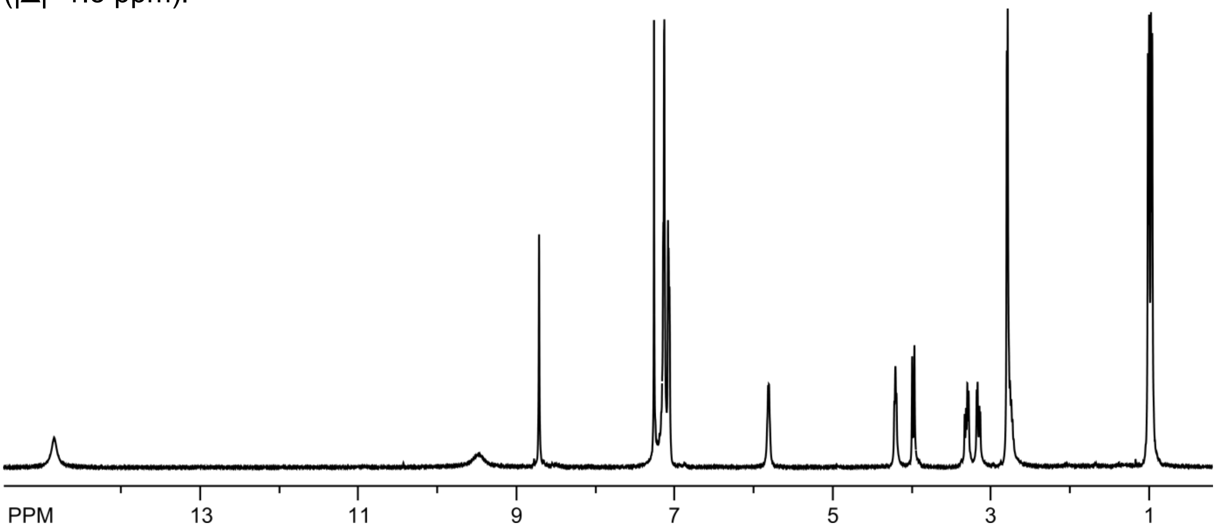


Figure S3. ^1H NMR spectrum of (*S*)-**2c** (400 MHz, $CDCl_3$).

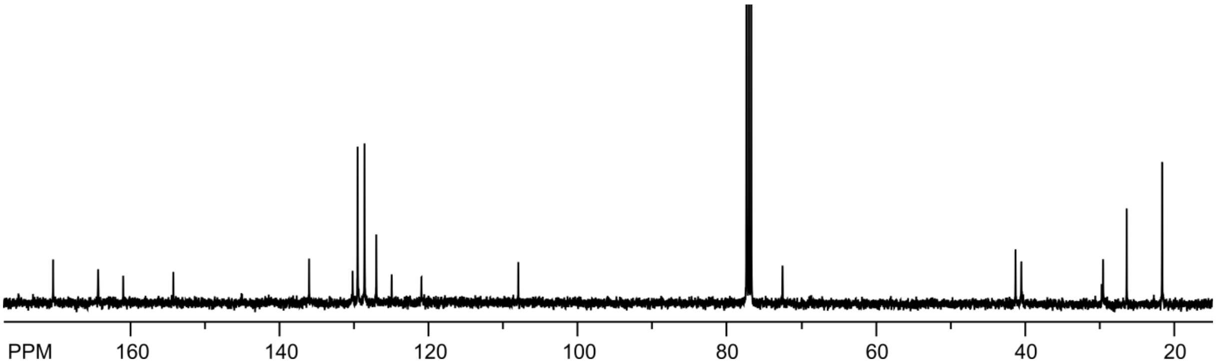
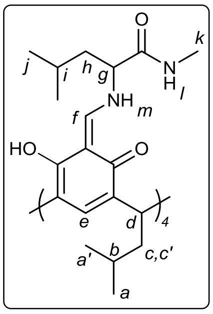


Figure S4. ^{13}C NMR spectrum of (*S*)-**2c** (100 MHz, $CDCl_3$).

(*S*)-2d

Was synthesized according to literature procedure (0.1 mmol of **1a** was used).[3] (123.7 mg, 93 %). (*S*)-**2d** is poorly soluble in chloroform. In DMSO it exists as a mixture of diastereoisomers.



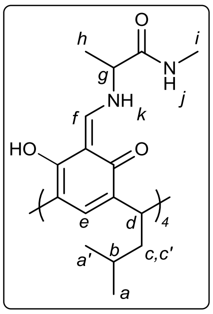
δ_H (400 MHz, DMSO-d_6) 14.27 (2 H, br s, *m*), 14.02 (2 H, br s, *m*), 11.80 (4 H, br s, OH), 8.62 (4H, br s, *f*), 8.19 (4 H, q, *J* 4.6, *l*), 7.43 (4 H, br s, *e*), 4.43 (4 H, t, *J* 7.8, *d*), 4.38-4.32 (4 H, br m, *g*), 2.60 (12 H, br s, *k*), 2.18-2.08 (4 H, br m, *c*), 2.04-1.94 (4 H, br m, *c'*), 1.71-1.55 (4 H + 4 H, br m + m, *b* + *i*), 1.49-1.39 (8 H, m, *h*), 0.94 (24 H, d, *J* 6.4, *j*), 0.90 (12 H, d, *J* 6.7, *a*), 0.87 (12 H, d, *J* 6.7, *a'*).

δ_C (100 MHz, DMSO-d_6) (171.5, 171.0, br), 169.5, 161.4, (154.4, 154.2, br), 132.4, 128.5 (br), (116.4, 116.6, br), 106.2, 62.2, 41.8, 41.3, 30.4, 26.0, 25.6, 24.1, 22.5, 21.8.

HRMS (ESI): *m/z* calc for $C_{76}H_{113}N_8O_{12}$ 1329.8478, found 1329.8459 (|Δ|=1.4 ppm).

(*S*)-2e

Was synthesized according to literature procedure (0.1 mmol of **1a** was used).[3] (103.4 mg, 89 %).



δ_H (400 MHz, DMSO-d_6) 14.06 (4 H, br s, *k*), 11.86 (4 H, br s, OH), 8.65 (4 H, br s, *f*), 8.16 (4 H, br q, *j*), 7.43 (4 H, s, *e*), 4.42 (4 H + 4 H, t + t, *d* + *g*), 2.61 (12 H, br s, *i*), 2.18-2.04 (4 H, br m, *c*), 1.92-2.04 (4 H, br m, *c*'), 1.48-1.41 94 H, m, *b*), 1.42 (12 H, d, *J* 6.8, *h*), 0.95 (12 H, d, *J* 5.6, *a*), 0.94 (12 H, d, *J* 6.0, *a'*).

δ_C (100 MHz, DMSO-d_6) 171.7, 170.0, 161.2, 154.3, 132.4, 128.7, 116.2, 106.2, 58.3, 40.4, 30.3, 26.0, 25.6, 22.73, 22.67, 19.8.

HRMS (ESI): *m/z* calc for $C_{64}H_{89}N_8O_{12}$ 1161.6600, found 1161.6595 (|Δ|=0.4 ppm).

NMR titration

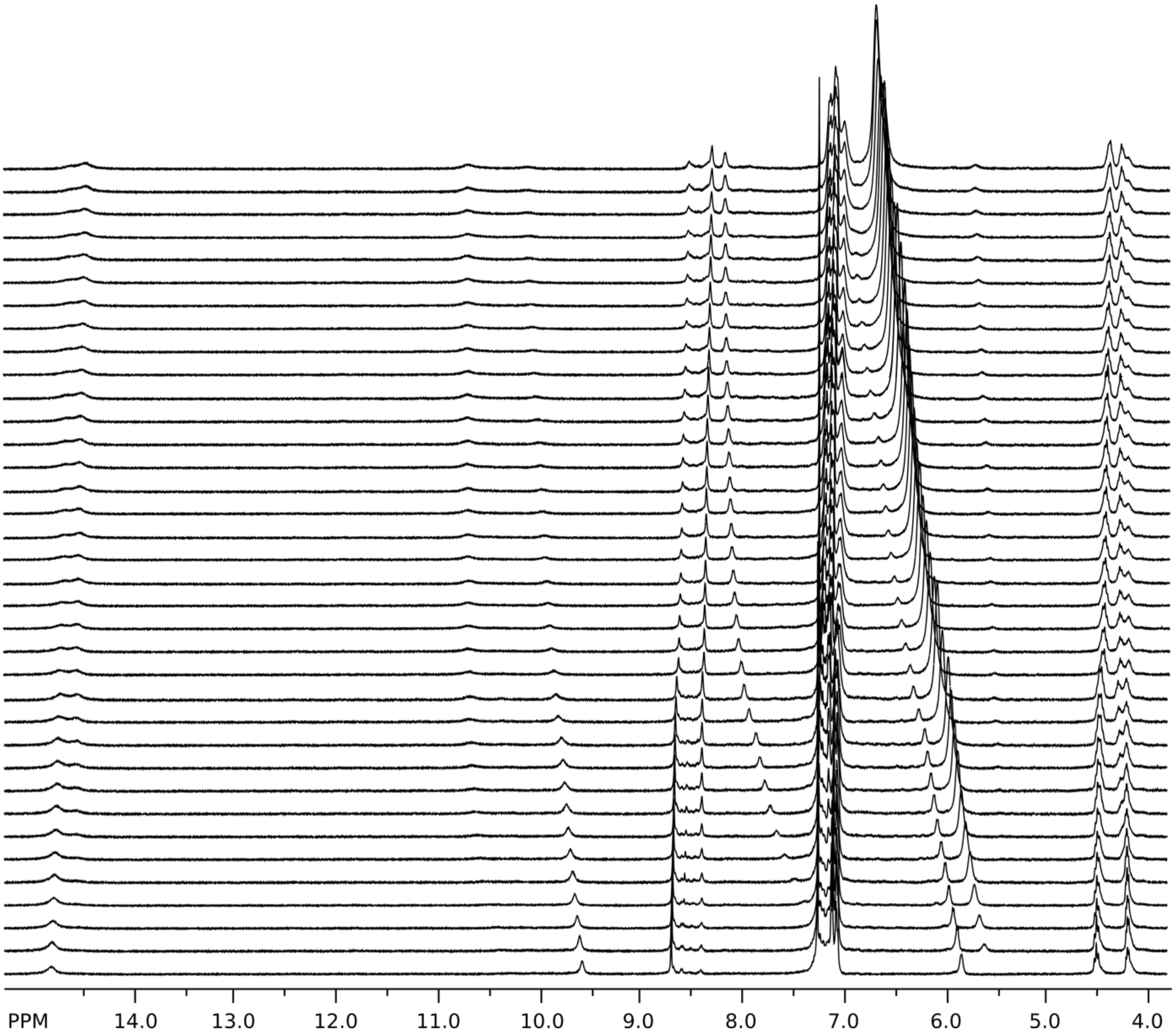


Figure S5. ^{1}H NMR spectra of (*S*)-**2a** titrated with **3** (400 MHz, $CDCl_3$, 298 K).

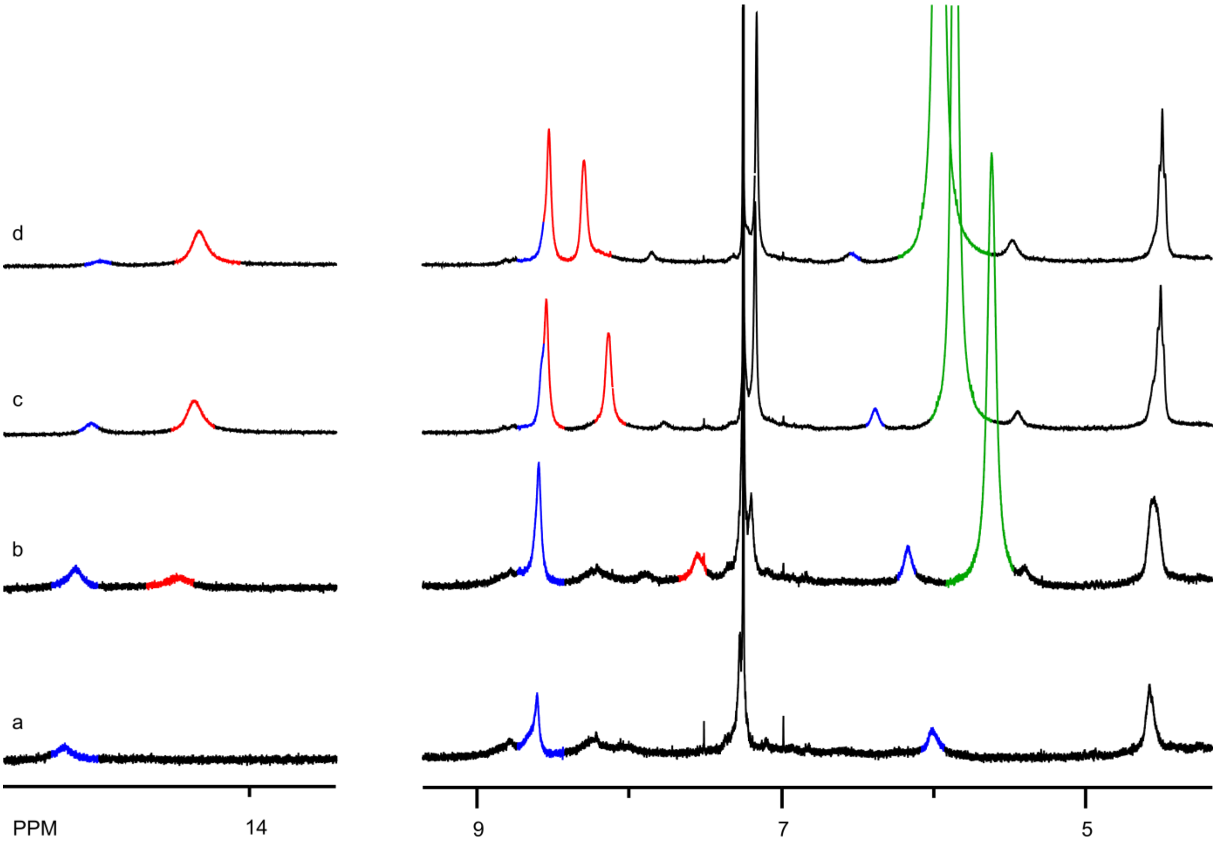


Figure S6. Partial ^{1}H NMR spectra of (*S*)-**2b** titrated with **3**; a) (*S*)-**2b** (13 mM); b) (*S*)-**2b** + **3** (6 equiv.); c) (*S*)-**2b** + **3** (15 equiv.); d) (*S*)-**2b** + **3** (23 equiv.). (*S*)-**2b** is poorly soluble in chloroform and only qualitative NMR titration was possible. The spectra show gradual transformation of (*M*,*S*)-**2b** (blue) into (*P*,*S*)-**2b** (red) upon addition of **3** (green) (400 MHz, $CDCl_3$, 298 K).

ECD titration

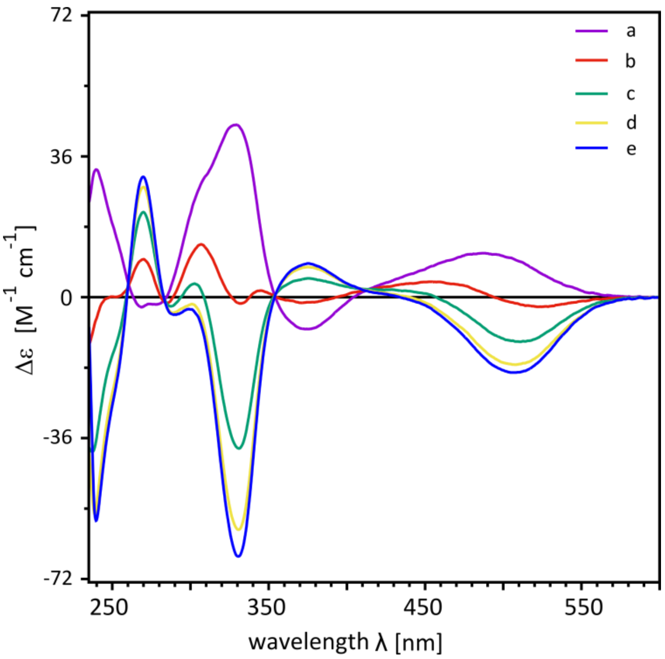
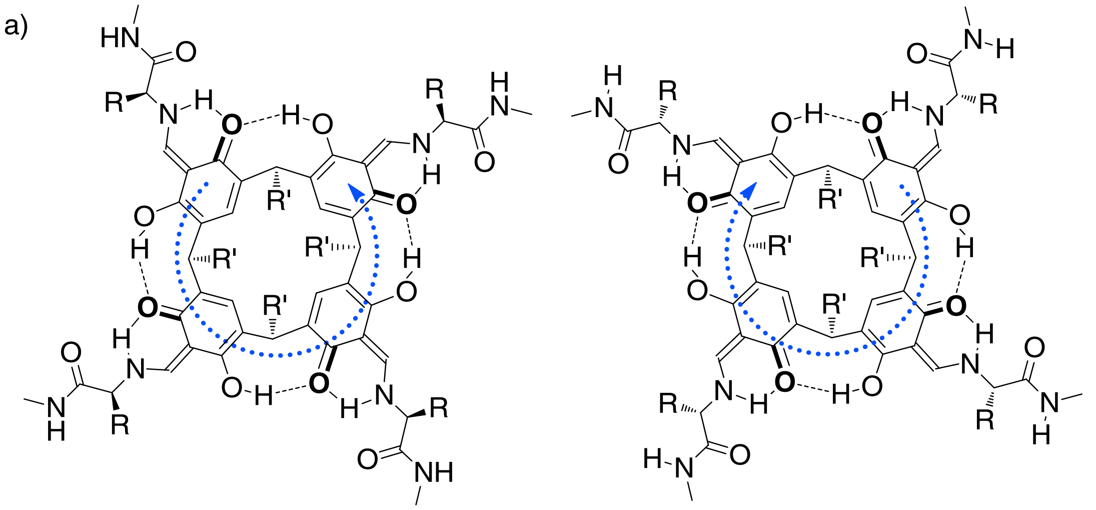


Figure S7. ECD titration of (*S*)-**2b** with **3** in CHCl$_3$ at 298 K (a – (*S*)-**2b** (0.1 mM), b – (*S*)-**2b** + **3** (75 mM), c – (*S*)-**2b** + **3** (143 mM), d – (*S*)-**2b** + **3** (262 mM), e – (*S*)-**2b** + **3** (408 mM)).

Ab initio calculations



(*M*,*S*)-**2f** R=CH_2Ph, R'=CH_3
(*M*,*S*)-**2g** R=$CH(CH_3)_2$, R'=CH_3

(*P*,*S*)-**2f** R=CH_2Ph, R'=CH_3
(*P*,*S*)-**2g** R=$CH(CH_3)_2$, R'=CH_3

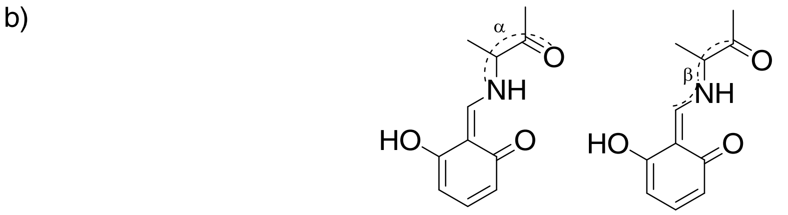


Figure S8. a) chemical structures of model compounds that were used for theoretical calculations; b) torsion angles that were varied during conformational search.

To simplify theoretical calculations some fragments of the original structures were modified and model compounds **2f** and **2g** were used for theoretical calculations (**Figure S8a**). Aliphatic chains at lower rim (R') were shortened since their lengths have negligible influence on UV-VIS and ECD spectra (Fig. 2a, compare compounds (*S*)-**2a** and (*S*)-**2c**)). (S)-**2g** has lower flexibility of the side chains than the other amino acids and lacks additional chromophores. The geometry of the initial structures was taken from the crystal structures of ((*S*)-**2a**)((*R*)-**2a**) and (*S*)-**2c** and optionally symmetrized to C_4 symmetric structure. Conformational search was performed by 60° rotation about two bonds (**Figure S8b**) and assuming C_4 symmetry (simplification based on the observed symmetry in NMR spectra). Using this approach 36 starting structures were generated, which converged into a set of eight conformations for each of the diastereoisomers (Tables below)

All calculations were performed within the density functional theory (DFT) approach using Gaussian 09 program suite.[4] Geometry was optimized with the B3LYP functional, employing the 6-31G(d,p) basis set. Solvent effects were considered within the SCRF theory using the polarized continuum model (PCM) approach to model the interaction with the solvent. Excited electronic states were determined at the B3LYP/6-31G(d) level by means of the time-dependent DFT (TD DFT) approach (100 excited states in each case). The ECD spectra were simulated by overlapping Gaussian functions for each transition where the width of the band at 1/e height is fixed at 0.16 eV and the resulting intensities of the combined spectra were scaled to the experimental values (using the lowest energy bands in UV-VIS spectra as references). Presentation of molecular orbitals was performed by using the GaussView program.

Table S1. Conformational analysis for (*M*,*S*)-**2g**.

input		output			
α	β	α	β	Conf. No. (population percentage)	ΔG [kcal/mol]
-45.85	-143.54	-40.9	-144.2	1 (72 %)	0
-105.85	-143.54	169.5	-109.4	2 (28 %)	0.56133728
-166.85	-143.54	169.5	-109.4	2	
134.15	-143.54	169.5	-109.4	2	
74.15	-143.54	169.5	-109.4	2	
14.15	-143.54	-40.9	-144.2	1	
-45.85	-83.54	-40.9	-144.2	1	
-105.85	-83.54	-40.9	-144.2	1	
-166.85	-83.54	169.5	-109.4	2	
134.15	-83.54	169.5	-109.4	2	
74.15	-83.54	-40.9	-144.2	1	
14.15	-83.54	-40.9	-144.2	1	
-45.85	-23.54	-41.5	-30.6	3 (< 0.01 %)	10.36314981
-105.85	-23.54	-41.5	-30.6	3	
-166.85	-23.54	169.5	-109.4	2	
134.15	-23.54	169.5	-109.4	2	
74.15	-23.54	169.5	-109.4	2	
14.15	-23.54	-41.5	-30.6	3	
-45.85	36.46	-57.5	41.0	4 (< 0.01 %)	8.93821671
-105.85	36.46	-57.5	41.0	4	
-166.85	36.46	-144.3	48.6	5 (< 0.01 %)	14.96899417
134.15	36.46	105.6	57.5	6 (< 0.01 %)	25.47607661
74.15	36.46	105.6	57.5	6	
14.15	36.46	-57.5	41.0	4	
-45.85	96.46	105.6	57.5	6	
-105.85	96.46	105.6	57.5	6	
-166.85	96.46	160.4	131.6	7 (< 0.01 %)	9.18290219
134.15	96.46	160.4	131.6	7	
74.15	96.46	160.4	131.6	7	
14.15	96.46	105.6	57.5	6	
-45.85	156.46	-40.9	-144.2	1	
-105.85	156.46	169.5	-109.4	2	
-166.85	156.46	169.5	-109.4	2	
134.15	156.46	158.7	150.0	8 (< 0.01 %)	9.55712705
74.15	156.46	-40.9	-144.2	1	
14.15	156.46	-40.9	-144.2	1	

Table S2. Conformational analysis for (*P*,*S*)-**2g**.

input		output			
α	β	α	β	Conf. No. (population percentage)	ΔG [kcal/mol]
-44.82	-135.87	-40.8	-139.5	1 (60.9 %)	0
-104.82	-135.87	-40.8	-139.5	1	
-164.82	-135.87	167.2	-103.9	2 (39.1 %)	0.26196
135.18	-135.87	167.2	-103.9	2	
75.18	-135.87	167.2	-103.9	2	
15.18	-135.87	-40.8	-139.5	1	
-44.82	-75.87	-40.8	-139.5	1	
-104.82	-75.87	-71.4	-88.9	3 (< 0.01 %)	4.53387804
-164.82	-75.87	167.2	-103.9	2	
135.18	-75.87	167.2	-103.9	2	
75.18	-75.87	167.2	-103.9	2	
15.18	-75.87	-40.8	-139.5	1	
-44.82	-15.87	-49.1	-7.0	4 (< 0.01 %)	3.88618118
-104.82	-15.87	-59.9	37.4	5 (< 0.01 %)	7.12466549
-164.82	-15.87	167.2	-103.9	2	
135.18	-15.87	167.2	-103.9	2	
75.18	-15.87	167.2	-103.9	2	
15.18	-15.87	-49.1	-7.0	4	
-44.82	44.13	-59.9	37.4	5	
-104.82	44.13	-147.0	49.7	6 (< 0.01 %)	10.47829592
-164.82	44.13	-147.0	49.7	6	
135.18	44.13	157.8	137.8	7 (< 0.01 %)	10.52147571
75.18	44.13	157.8	137.8	7	
15.18	44.13	-59.9	37.4	5	
-44.82	104.13	-59.9	37.4	5	
-104.82	104.13	167.2	-103.9	2	
-164.82	104.13	157.8	137.8	7	
135.18	104.13	157.8	137.8	7	
75.18	104.13	157.8	137.8	7	
15.18	104.13	-40.8	-139.5	1	
-44.82	164.13	-40.8	-139.5	1	
-104.82	164.13	167.2	-103.9	2	
-164.82	164.13	167.2	-103.9	2	
135.18	164.13	157.8	137.8	7	
75.18	164.13	-40.8	-139.5	1	
15.18	164.13	-40.8	-139.5	1	

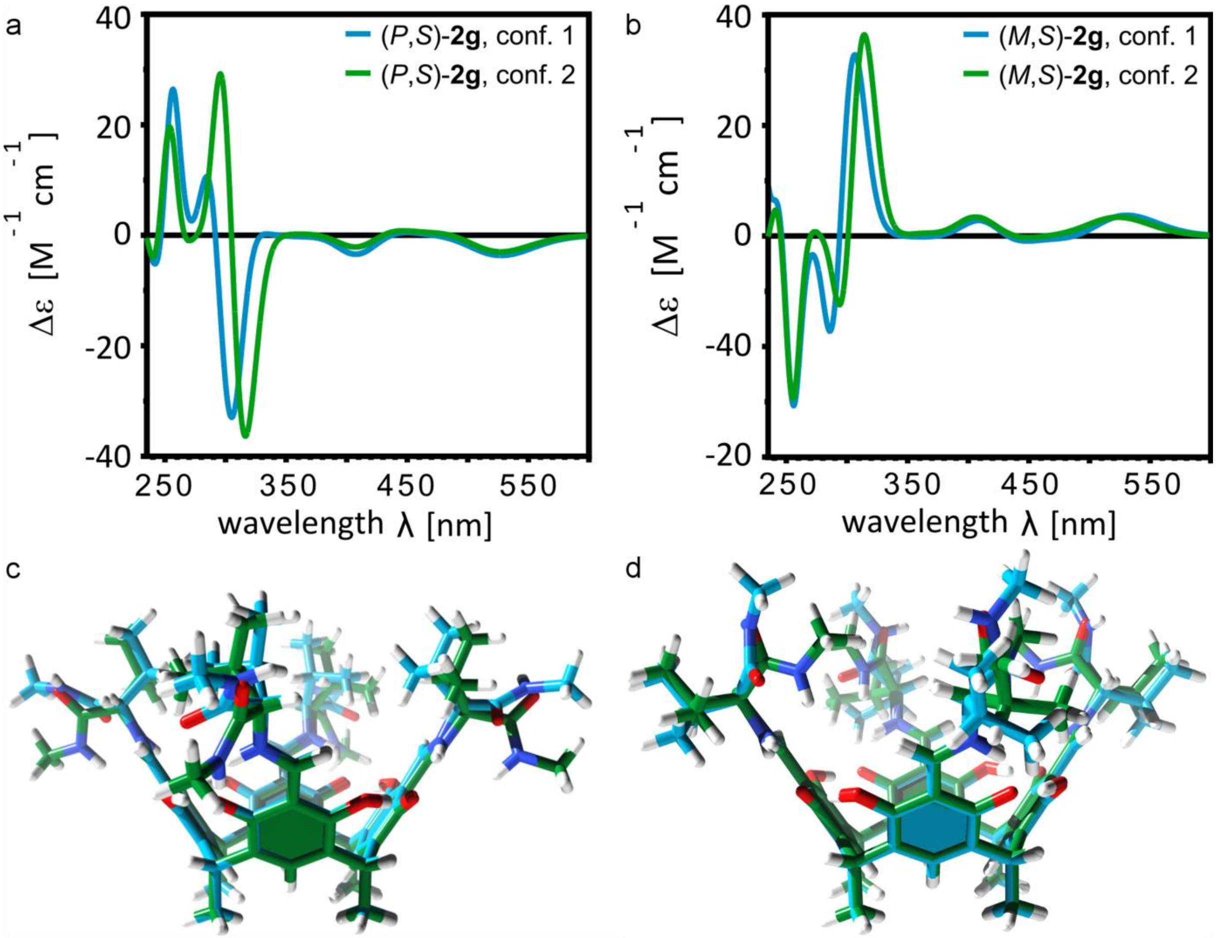


Figure S9. TD DFT calculated ECD spectra of different conformers of (*S*)-**2g** (a,b); comparison of conformers of (*P*,*S*)-**2g** (c) and (*M*,*S*)-**2g** (d).

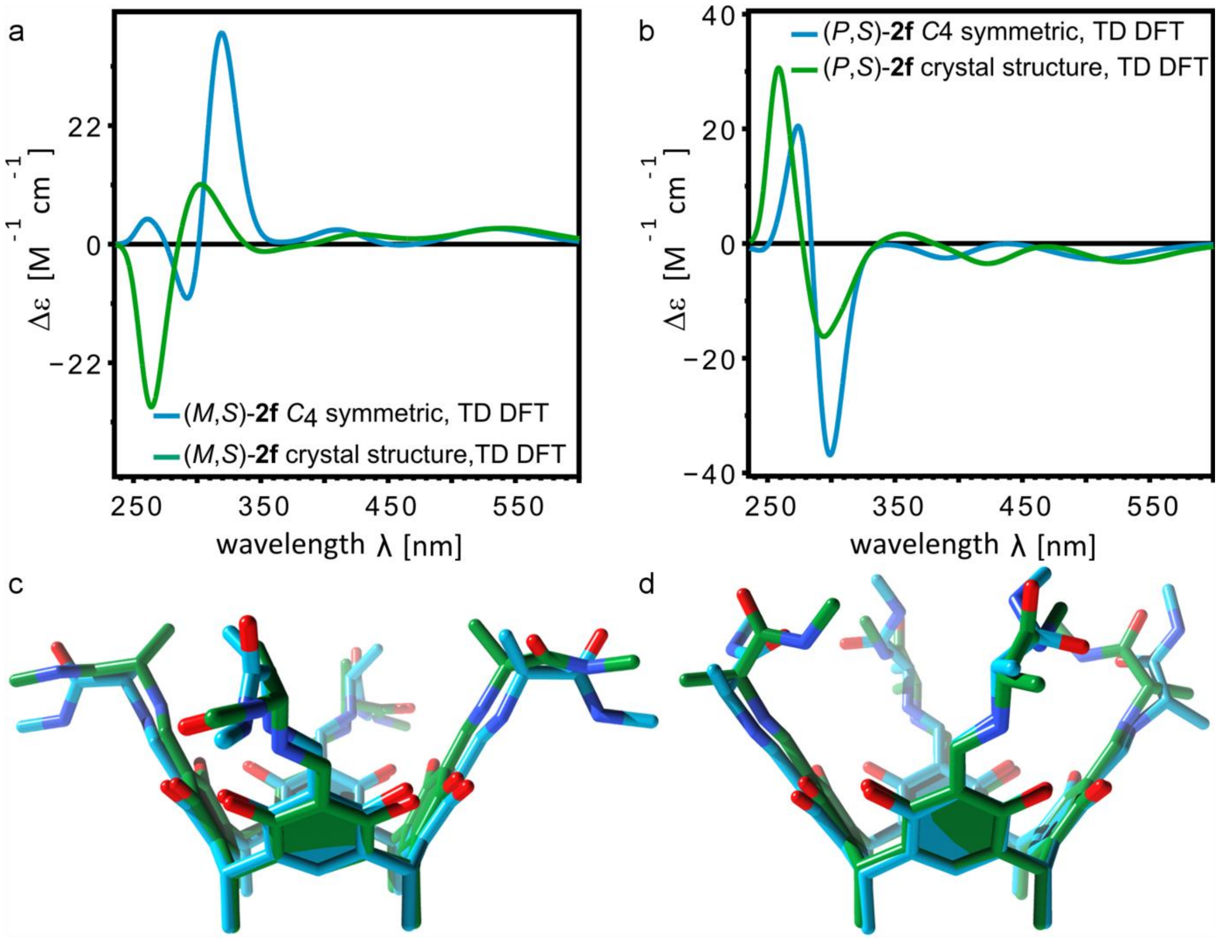


Figure S10. Influence of symmetry on ECD spectra. Comparison of C_4 symmetric and C_1 symmetric conformers of: (a, b) (*M*,*S*)-**2f** (RMSD = 1.099 Å) and (c, d) (*P*,*S*)-**2f** (RMSD = 1.245 Å).

Crystallographic data

CCDC 1405961 contains the supplementary crystallographic 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.

Table S3. Crystal data for (*S*)-**2c**.

Crystal data	
Moiety formula	((*S*)-**2c**)·(ethyl acetate)$_{2.5}$
Empirical formula	$(C_{84}H_{96}N_8O_{12})\cdot(C_4H_8O_2)_{2.5}$
Formula weight	1629.95
Temperature (K)	99.97(15)
Wavelength (Å)	1.54178
Crystal system	monoclinic
Space group	$P\ 2_1$
Unit cell dimensions a/b/c (Å)	18.7521(4) 23.0271(4) 25.3314(4)
Unit cell angles α/β/γ (°)	90 89.8645(19) 90
Unit cell volume (Å^3)	10938.2(4)
Z	4
Calculated density (g/cm^3)	0.990
Absorption coefficient (mm^{-1})	0.551
F(000)	3488
θ range for data collection (°)	70.26 – 3.50
Index ranges	$-22 < h < 22$ $-28 < k < 26$ $-30 < l < 30$
Reflections collected	145750
Independent reflections	37151 (R_{int} = 0.1170)
Completeness to θ_{max}	0.994
Refinement statistics	
Final R indices [$>2\sigma(I)$]	0.0677
R indices [all data]	0.0991
Goodness-of-fit	0.907
Extinction coefficient	-
Largest diff. peak and hole (e Å^{-3})	0.304 / -0.291

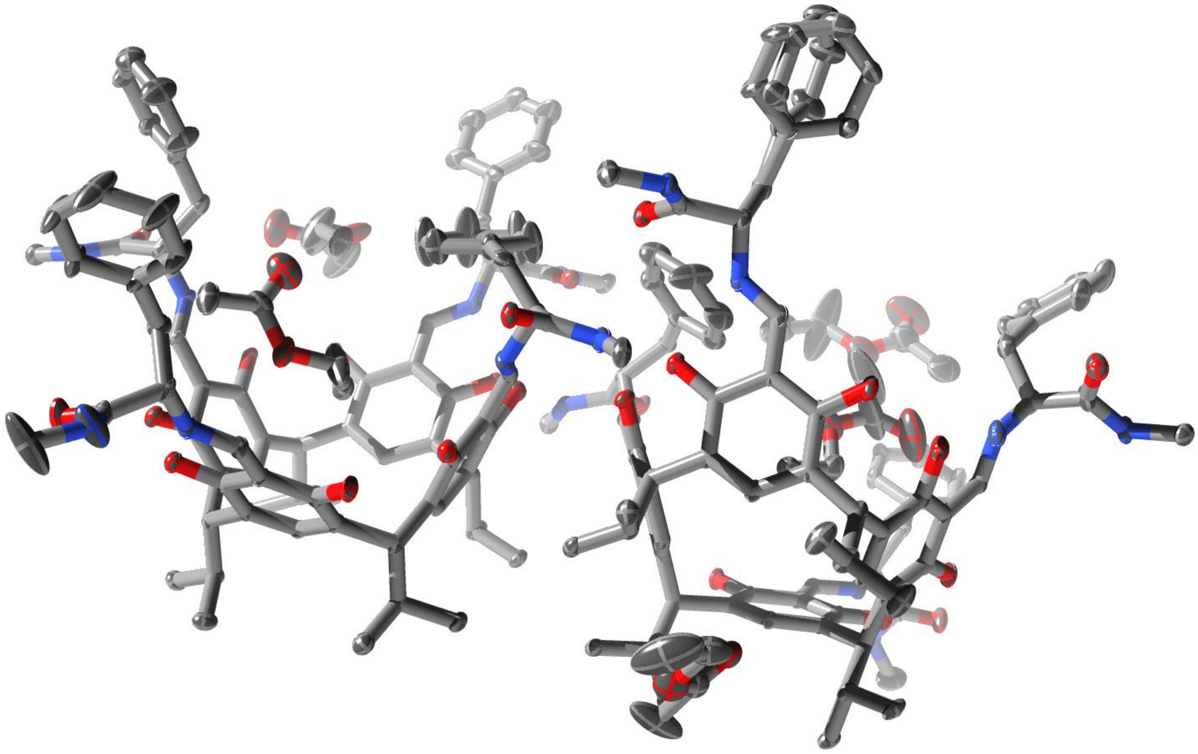


Figure S11. ORTEP representation of crystallographically independent part of (*S*)-**2c**. Thermal ellipsoids are depicted at 50% probability. Hydrogen atoms removed for clarity.

References

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[3] H. Jędrzejewska, M. Wierzbicki, P. Cmoch, K. Rissanen and A. Szumna, *Angew. Chem. Int. Ed.*, 2014, **53**, 13760.

[4] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.