

Supporting Information

Triphenylamine-based rhombimine macrocycles with solution interconvertible conformation

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Materials

Triphenylamine (Aldrich, 97%) and (1R,2R)-trans-1,2-diaminocyclohexane (**2**) (Aldrich, 98%) were used as received. Solvents were purchased from Aldrich source and were dried using the usual procedures. All manipulations of air/moisture-sensitive materials were handled under nitrogen atmosphere. 4,4'-Diformyl triphenylamine (**1a**) was synthesized by formylation of triphenylamine in presence of high excess of POCl₃/DMF mixture [1,2]. Other derivatives: 4,4'-bis formyl 4''-bromo triphenylamine (**1b**) [3] and 4,4',4''-tris(p-formylphenyl)amine (**1c**) [1,2] were synthesized and purified according to the reported methods.

Instrumentations

The FT-IR spectra were recorded in KBr pellets on a Bruker Vertex 70 spectrometer, while UV-vis absorption spectra were obtained on a Specord 200 Analytik Jena spectrophotometer using 10 mm quartz cells. ¹H-NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz) as solutions in CDCl₃ and chemical shifts are reported in ppm and referred to TMS as internal standard. MS measurements were performed with a Mass Spectrometer model ESI-Q-ToF-MS Agilent 6520 (Electrospray Ionization Quadrupole–Time of Flight) and methanol/chloroform (1:3) as solvent. Thermal gravimetric analysis (TGA) was performed by means of a Mettler Toledo TGA-SDTA 851e device, in N₂ atmosphere, with a flow of 20 ml/min, and a heating speed of 10 K/min (25-850 °C range). DSC measurements were performed with a Mettler DSC-12E apparatus, in nitrogen.

Experimental

Synthesis of rhombimines

(2R,3R,17R,18R)-1,4,10,16,19,25-hexaaza-10,25-diphenyl-(2,3:17,18)-dibutano-(6:9,11:14,21:24,26:29)-tetraetheno-(2H,3H,17H,18H)-tetrahydro-(30)-annulene (3a):

A solution of dialdehyde **1a** (0.4457 g, 1.48 mmol) in CH₂Cl₂ (5 ml) was added to a solution of *(1R,2R)-trans*-1,2-diaminocyclohexane **2** (0.1691 g, 1.48 mmol) in 5 ml dried CH₂Cl₂ (20 mL) at room temperature and nitrogen atmosphere and stirred for 5 hours under gentle reflux. The solvent was evaporated and the crude product was completely dissolved in N,N-dimethylformamide at reflux and by fast cooling a gel-like system was obtained that was filtered to give colorless fine powder of **3a** in 85.7 % yield (0.48 g). Mp=325 °C (with decomposition).

¹H-NMR (crude product) (CDCl₃): 8.11 and 7.91 ppm (*CH=N*), 6.9-7.5 ppm (26H, aromatic protons from triphenyl amine rings), 3.35-3.22; 2.04; 1.87; 1.48 ppm (from cyclohexane) δ= 7.34 (d, J=8.8 Hz, 8H, nitrogen *meta* aromatic protons in =CH-C₆H₄-N-), 7.24 (t, J=8.0 Hz, 4H, *meta* protons in -N-C₆H₅), 7.03-7.06 (m, 6H, *ortho* and *para* protons in -N-C₆H₅), 6.97 (d, J=8.8 Hz, nitrogen *ortho* aromatic protons in =CH-C₆H₄-N), 3.22-3.24 (m, 4H, -CH-N=), 2.05 (d, J=11.6 Hz, 4H of C₆H₁₀ ring), 1.88 (d, J=7.6 Hz, 8H of C₆H₁₀ ring) and 1.48 (q, J=10.4 Hz, 4H of C₆H₁₀ ring)

ESI-MS (m/z): 759.28: Calcd for C₅₂H₅₀N₆ =758. CHN (Found: C, 81.10; H, 6.78; N, 11.41. C₅₂H₅₀N₆ requires: C, 82.32; H, 6.60; N, 11.08.

Other imine macrocycles (**3b**, **3c**) were synthesized by the same procedure.

(2R,3R,17R,18R)-1,4,10,16,19,25-hexaaza-10,25-di(p-bromophenyl)-(2,3:17,18)-dibutano-(6:9,11:14,21:24,26:29)-tetraetheno-(2H,3H,17H,18H)-tetrahydro-(30)-annulene (3b):

Yield = 89.2 %. Recrystallized from tetrahydrofuran. $^1\text{H-NMR}$ (CDCl_3): 7.93 ppm (4H, $\text{CH}=\text{N}$) 7.5-6.8 ppm (24H, aromatic protons), 3.24; 2.04; 1.88 and 1.48 (20H, from cyclohexane). ESI-MS (m/z): 917.10 calcd for $\text{C}_{52}\text{H}_{48}\text{Br}_2\text{N}_6$ =916. CHN (Found: C, 66.38; H, 5.51; N, 9.06; Br, 16.91. $\text{C}_{52}\text{H}_{48}\text{Br}_2\text{N}_6$ (requires: C, 68.12; H, 5.24; N, 9.17; Br, 17.47).

(2R,3R,17R,18R)-1,4,10,16,19,25-hexaaza-10,25-di(p-formylphenyl)-(2,3:17,18)-dibutano-(6:9,11:14,21:24,26:29)-tetraetheno-(2H,3H,17H,18H)-tetrahydro-(30)-annulene (3c): Yield = 74.5 %

$^1\text{H-NMR}$ (CDCl_3) (crude product): 9.80 (2H, CHO), 8.14-7.90 ppm (4H, $\text{CH}=\text{N}$), 7.6-6.9 ppm (24H, aromatic protons), 3.38-3.32; 1.92 and 1.49 ppm (20H, from cyclohexane). ESI-MS (m/z): 816.35 Calcd for $\text{C}_{54}\text{H}_{50}\text{N}_6\text{O}_2$ (815). CHN (Found: C, 77.3; H, 6.11; N, 10.20. $\text{C}_{54}\text{H}_{50}\text{N}_6\text{O}_2$ requires: C, 79.55; H, 6.17; N, 10.34; O, 3.94).

Rhombamine derivative (**4a**) was obtained by reduction of the corresponding rhombimine (**3a**) with NaBH_4 in THF/methanol mixture and product was separated by precipitation in water. $^1\text{H-NMR}$ (CDCl_3): 7.3-6.9 ppm (26H, aromatic protons), 4.0-3.5 ppm (8H, $-\text{CH}_2-$), 2.4-1.0 ppm (12H, $-\text{NH}-$ and cyclohexane).

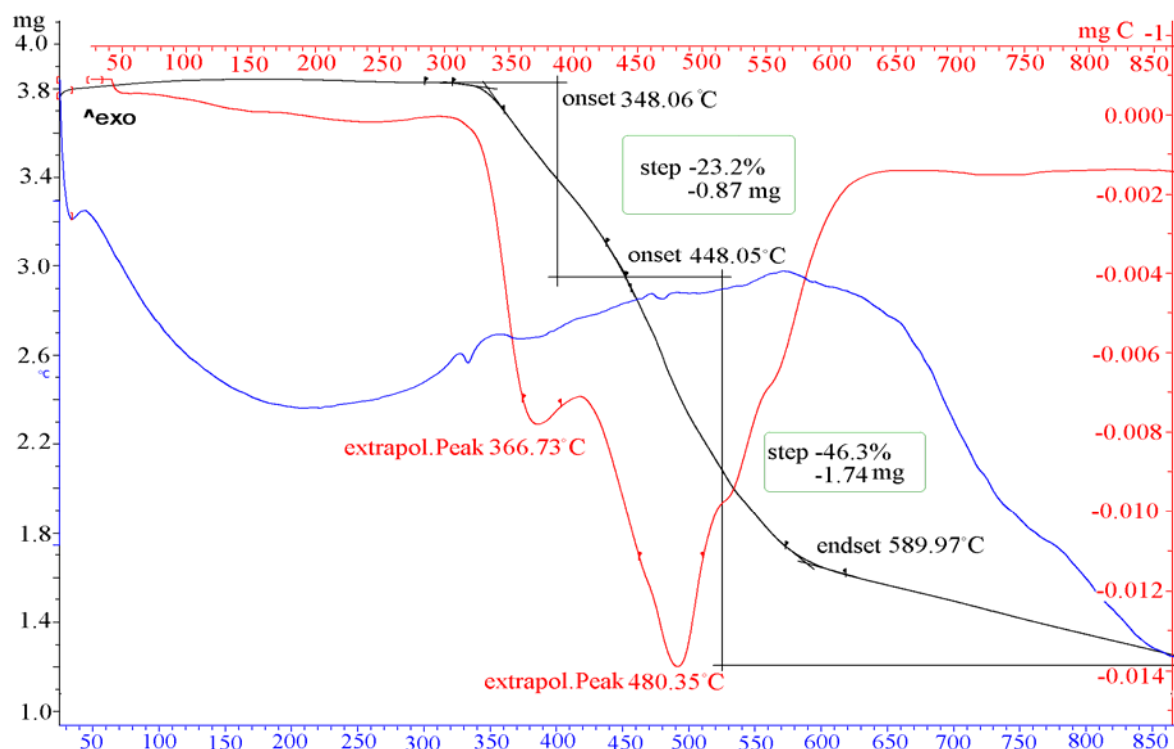


Figure S1. TG, DTG and DTA curves for **3a**.

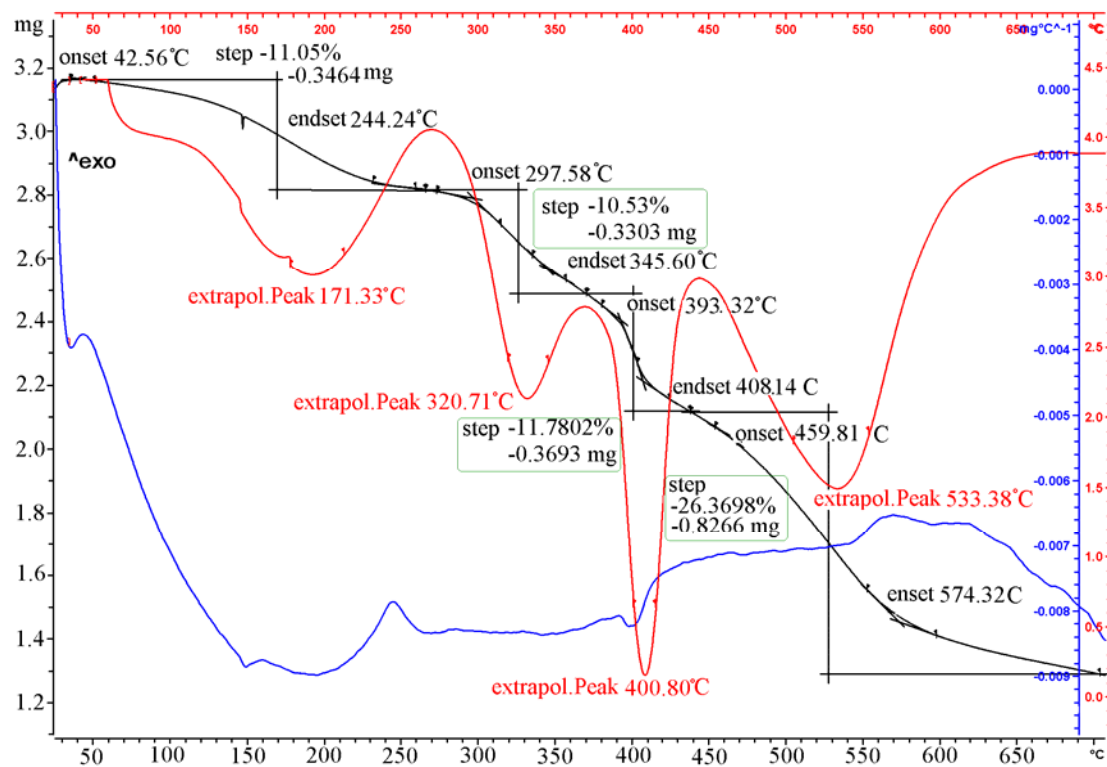


Figure S2. TG, DTG and DTA curves for **3b**.

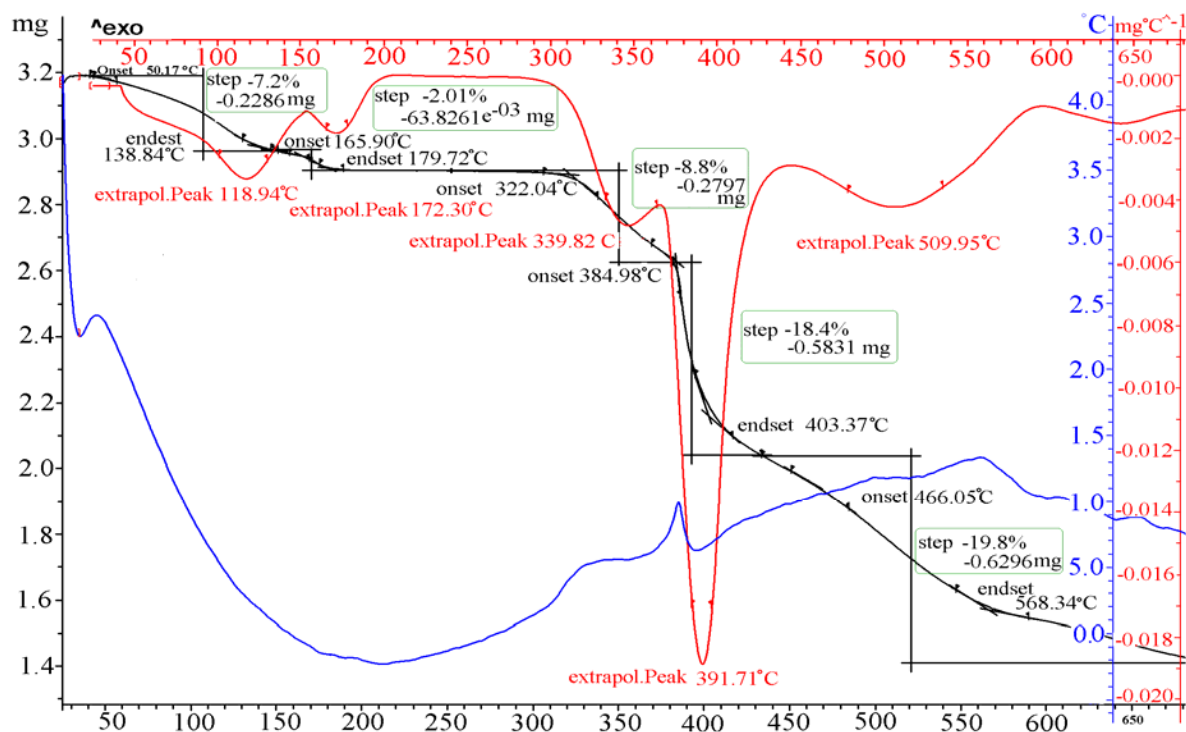


Figure S3. TG, DTG and DTA curves for **3c**.

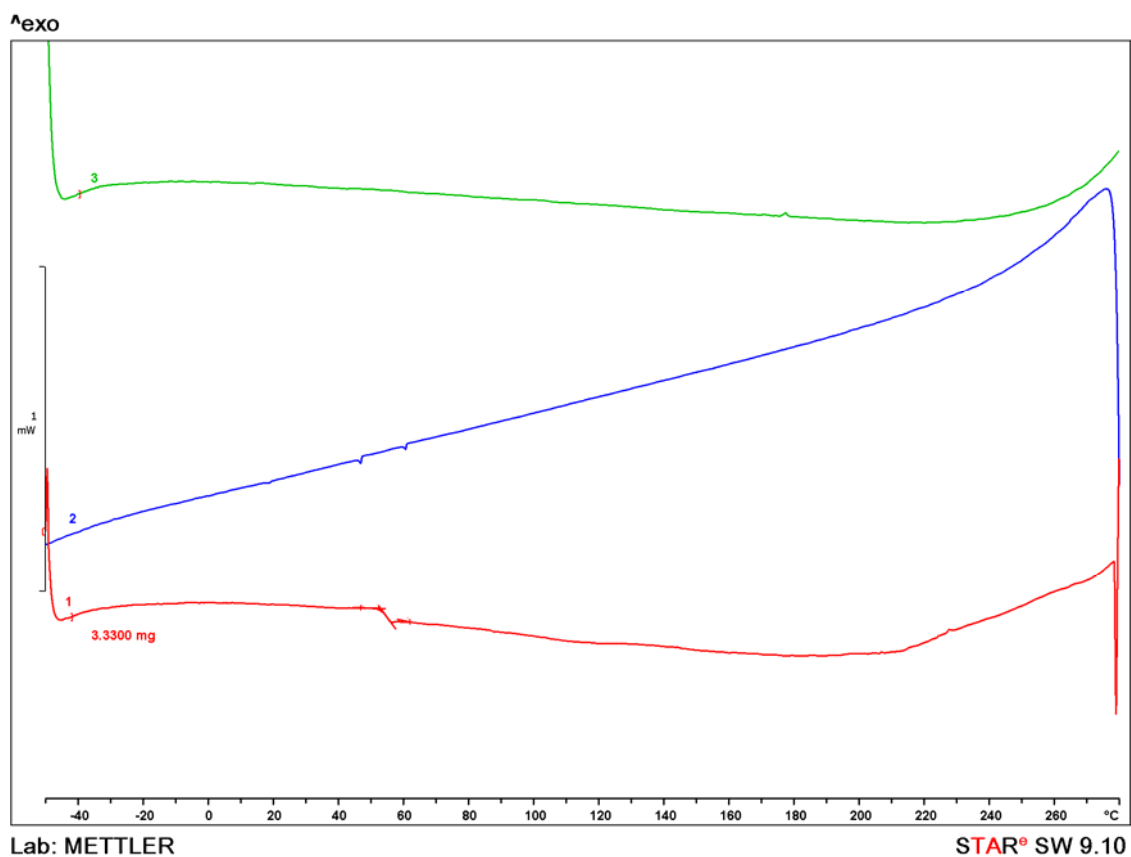


Figure S4. DSC runs for **3a** (heating and cooling rate 10K/min, nitrogen): 1) first heating, 2) first cooling, and 3) 2-nd heating

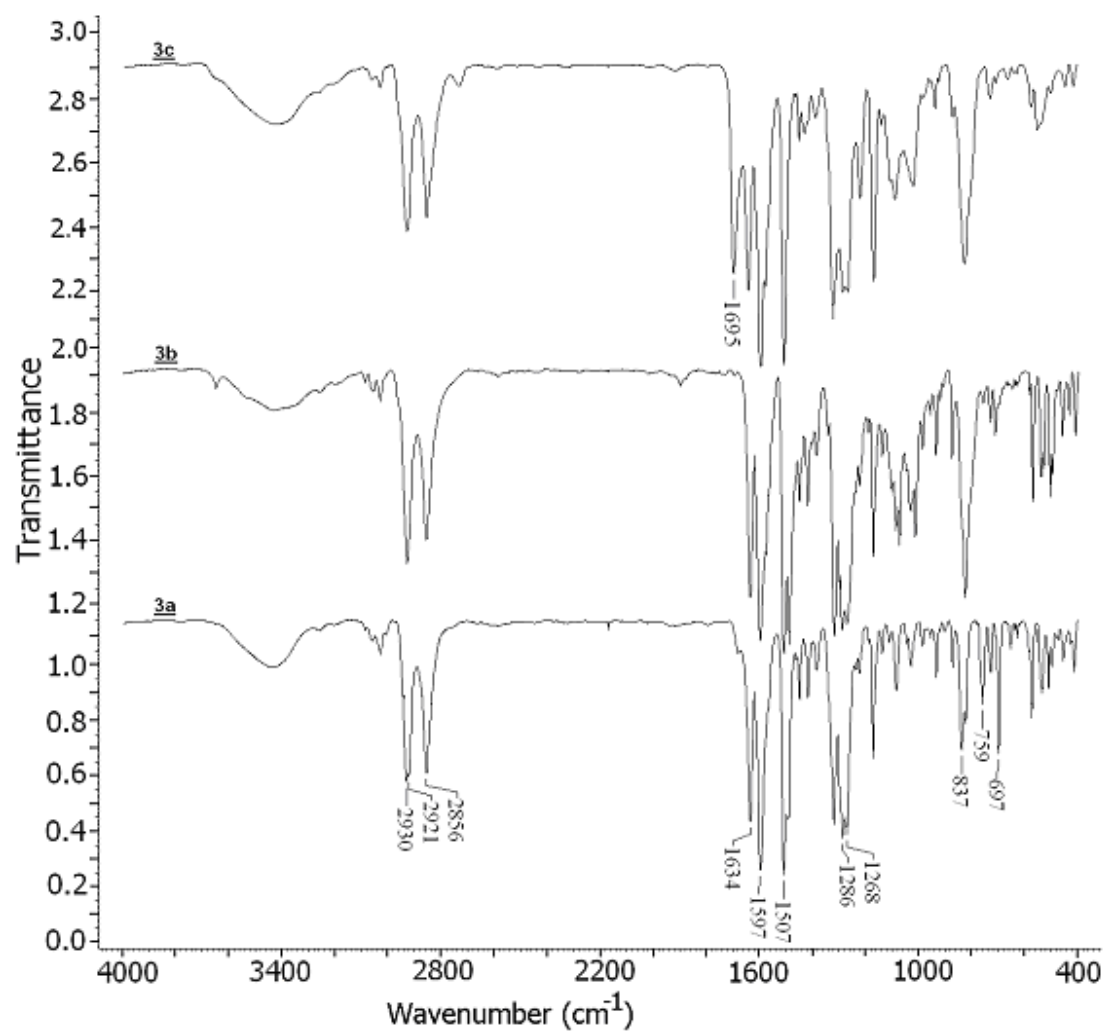


Figure S5: FTIR spectra of triphenylamine-based rhombimines (KBr pellets).

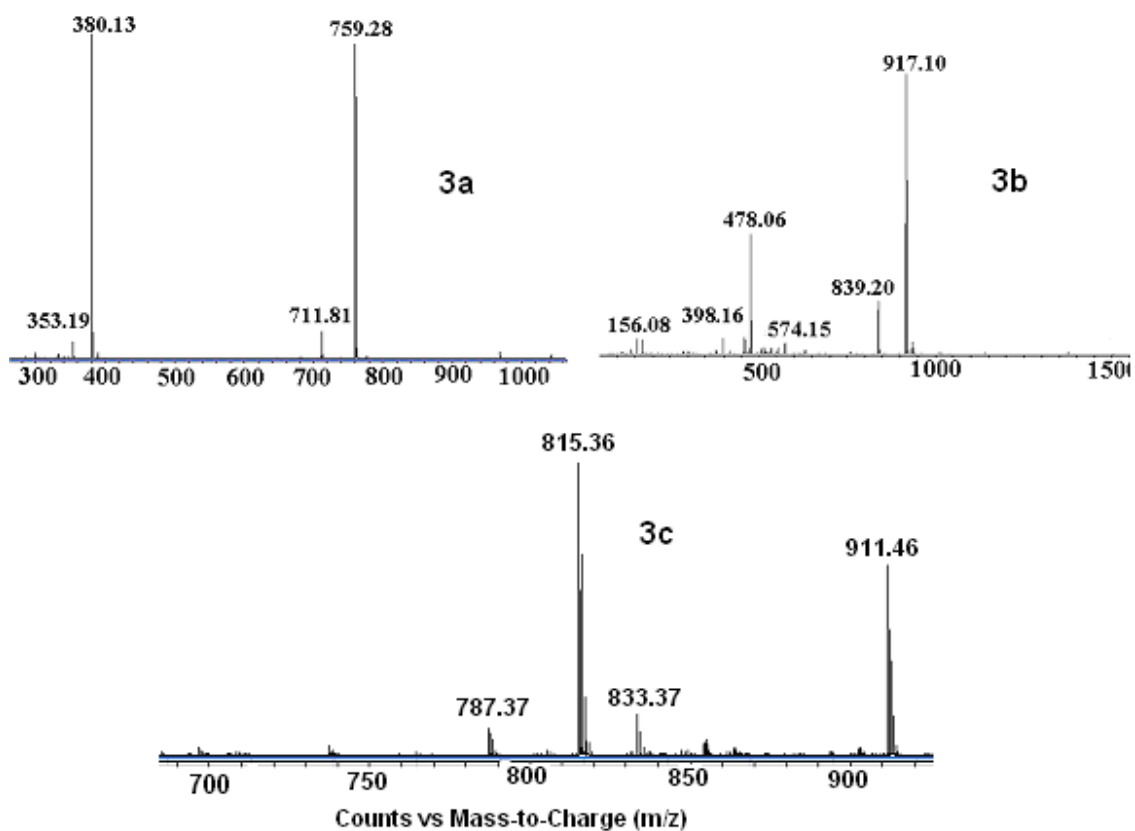
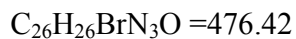
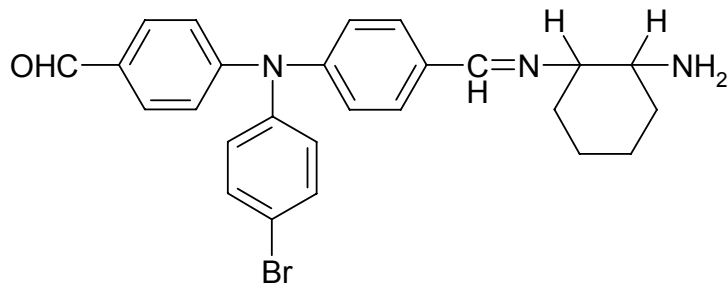
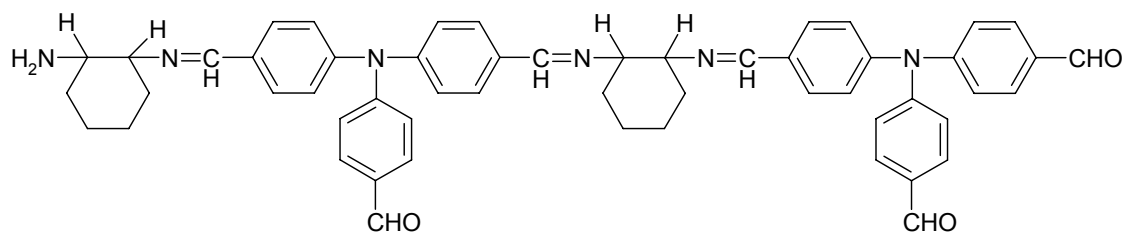


Figure S6: ESI-MS for **3a**, **3b** and **3c**

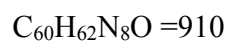
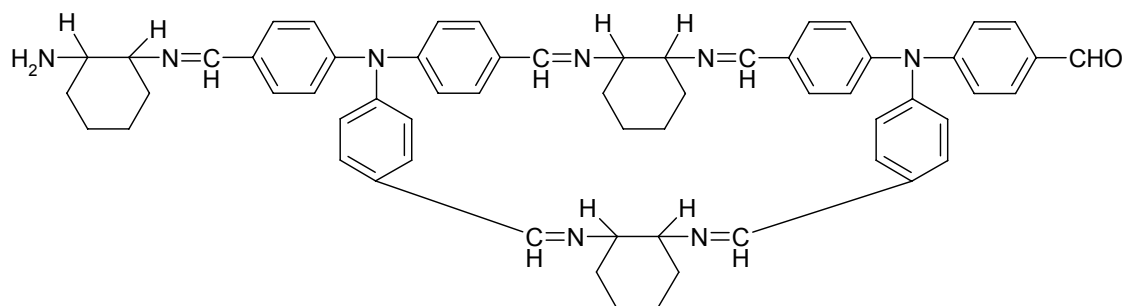
3b: The peak at 478.06 Da could be assigned to the linear [1+1] compound



3c: The signal positioned at 833.37 Da could be associated to the linear compound ($M=832$), remained as side product from the cyclization step or resulted from hydrolysis of macrocycle **3c**.



The peak at 911.461 Da could be associated to the [2+3] semi-linear compound having the structure:



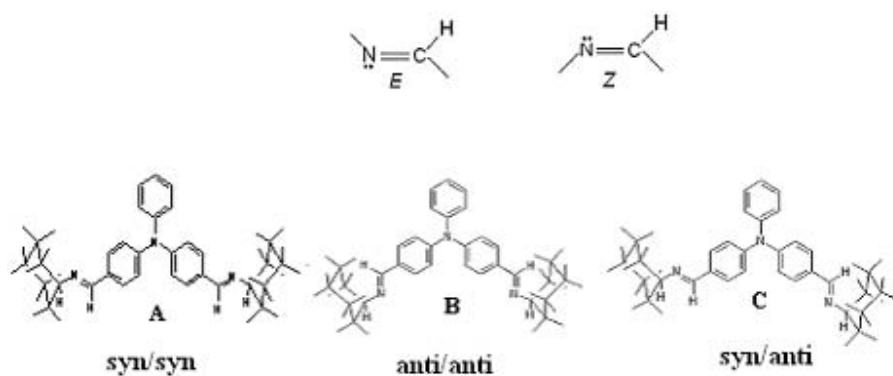


Figure S8. E/Z and *syn/anti* isomers

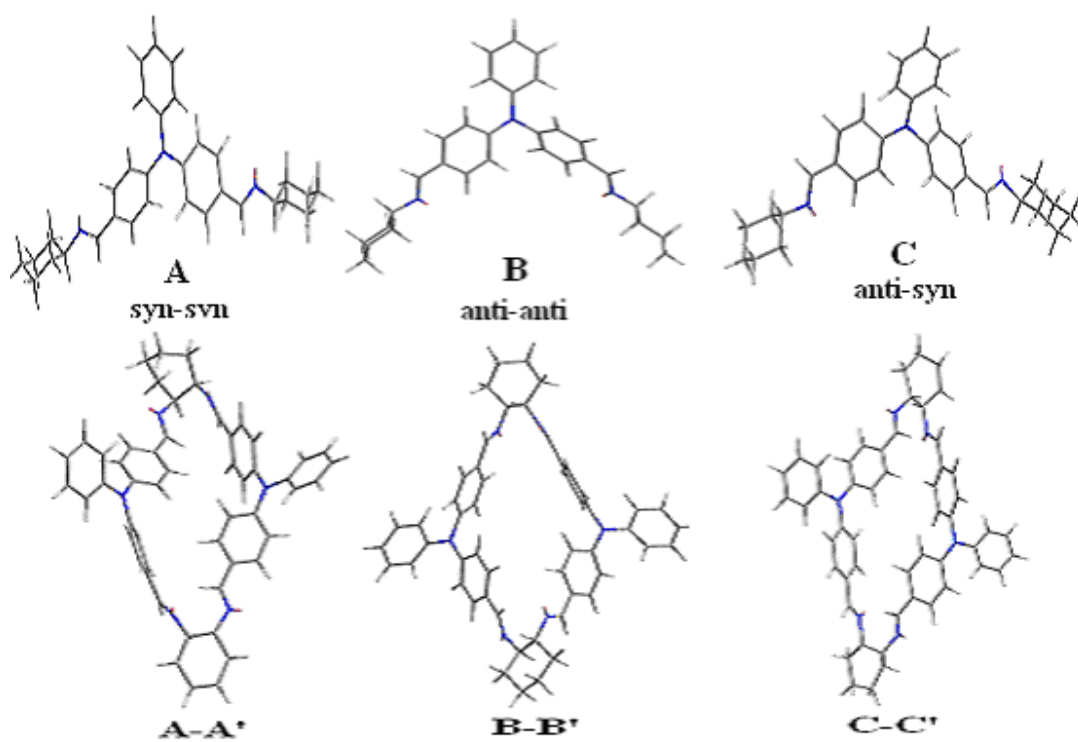


Figure S9. Stereoplot of the MMX force field minimized structure of A, B and C fragments and three macrocycle conformers

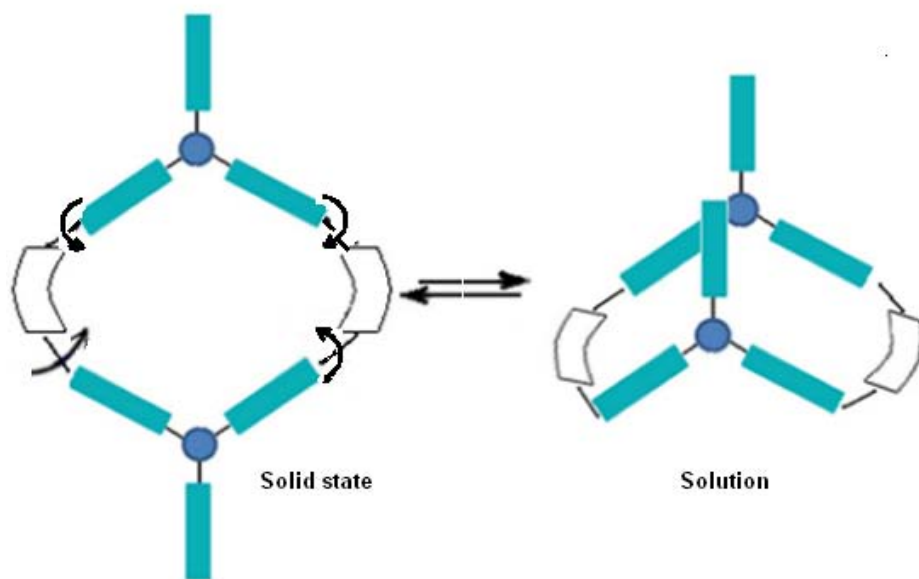


Figure S10. Schematic representation of conformational modification of macrocycle **3a**, **3b** and **3c**

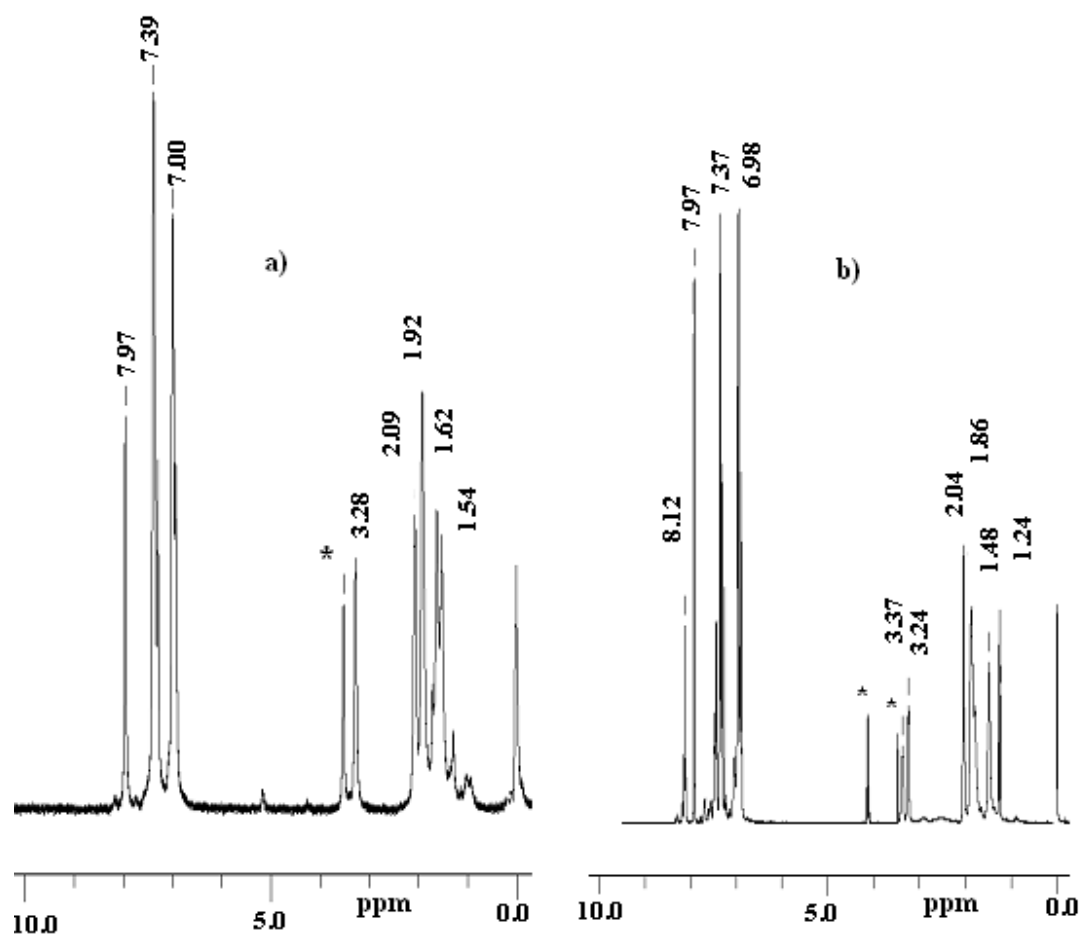


Figure S11. $^1\text{H-NMR}$ spectrum of **3b** recrystallized (a), and after isomerization (b)
*)signals due to impurities.

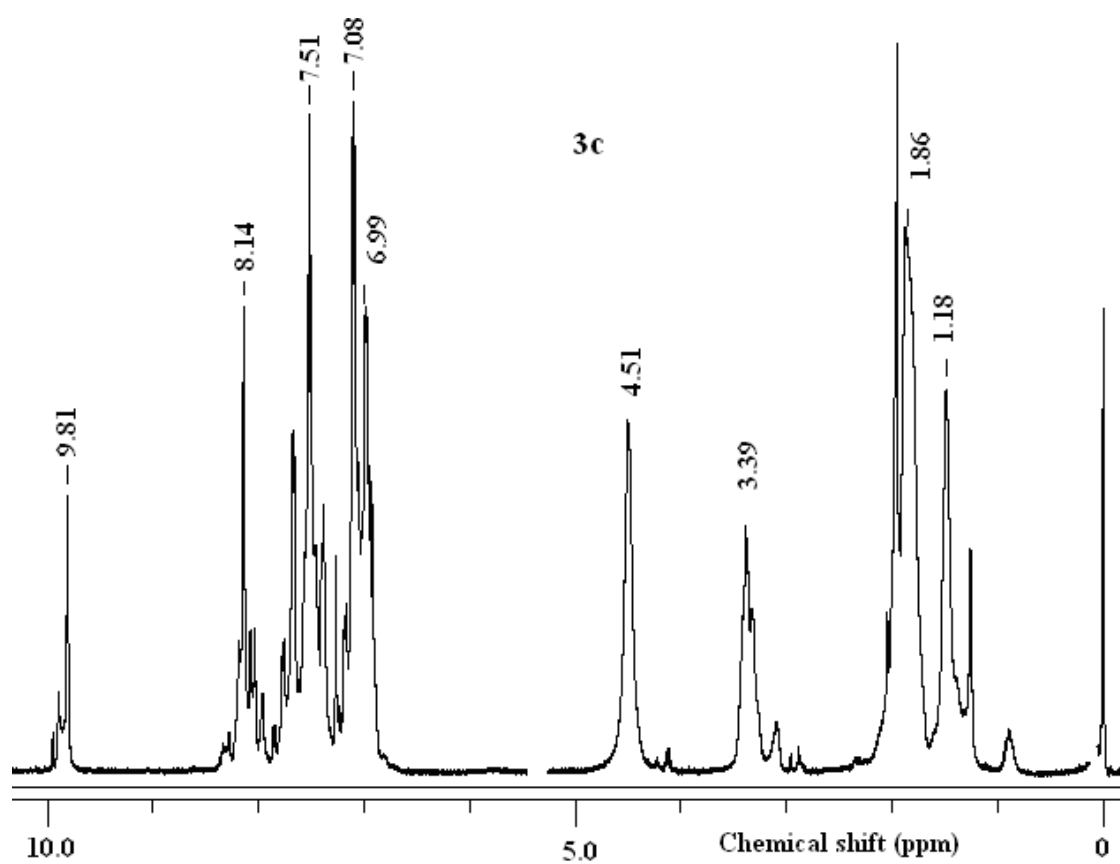


Figure S12. ¹H-NMR spectrum of 3c.

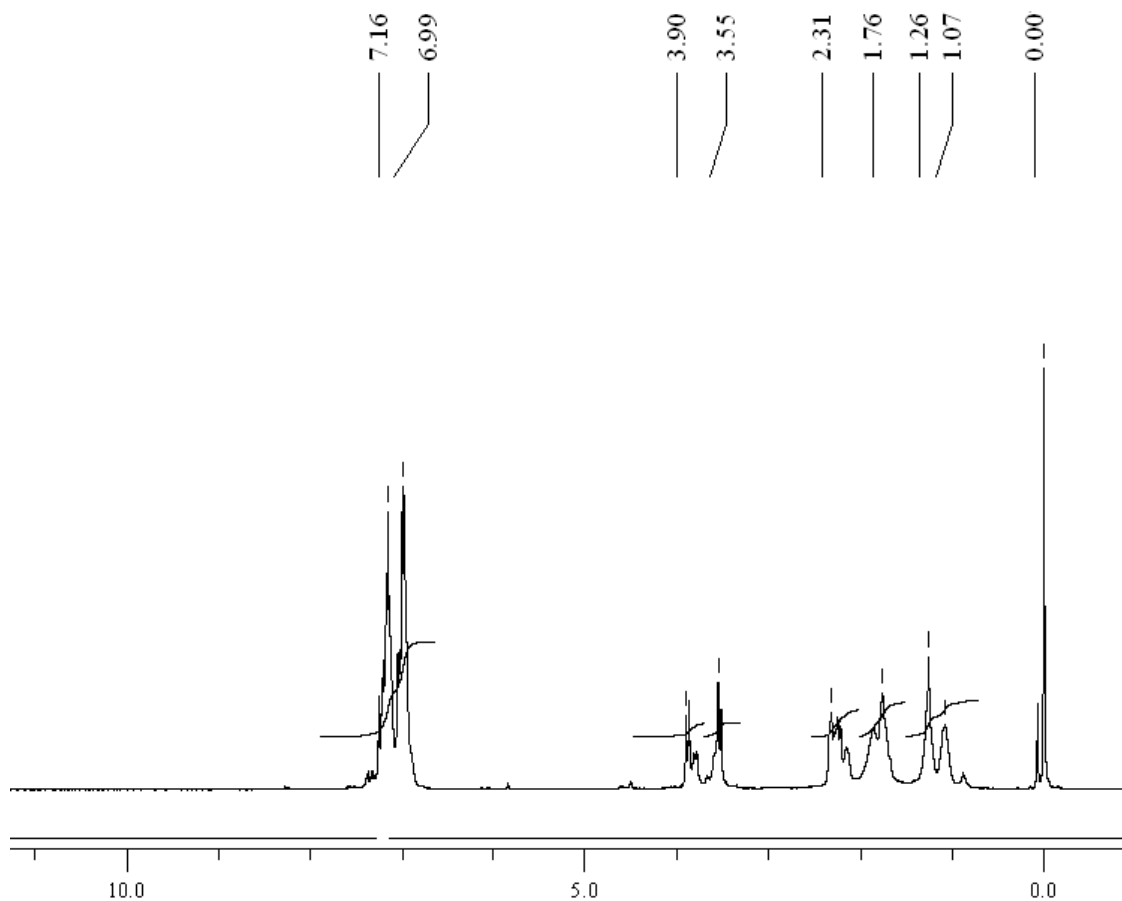


Figure S13. $^1\text{H-NMR}$ spectrum (CDCl_3) of rhombamine **4a**

References

1. M. Grigoras and L. Stafie, *Des. Mon. Polym.*, 2009, **12**, 177-196.
2. T. Mallejol, S. Gmoh, M. A. A. Meziane, M. Blanchard-Desce and O. Mongin, *Synthesis*, 2005, **11**, 1771-1774.
3. G. K. Paul, J. Mwaura, A. A. Argun, P. Taranekar and J. R. Reynolds, *Macromolecules*, 2006, **39**, 7789-7792.