Supporting Information for

"Novel Nitrogen-rich Energetic Macromolecules Based on Dihydrazinyl-Tetrazine"

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Table S1: the dependence of formed cycle sizes on the temperature

T / °C	DHTZ-HM	DHTZ-TM	DHTZ-DMB
20	2	2	2
40	2	2	1,2,3
55	1,2,3	1,2,3	1,2,3
70	1,2,3	1,2,3	1,2,3
100	1,2,3	1,2,3	1,2,3
Reaction conditions	A	B	A

Notes: method A, 1 mmol diisocyanate was added to a solution of 1 mmol of 3,6-dihydrazinyl-1,2,4,5-tetrazine (DHT) in 30 ml DMF/THF mixture with volume ratio of 1:1. The reactants were stirred for 2 days at the proposed temperatures. The obtained precipitates were filtered and dried; method B, 5 mmol of diisocyanate was added to the solution of 5 mmol of DHT in 30 ml DMF. The reactants were stirred for 48 hr at the mentioned temperature, and then the precipitates were filtered and dried.

Table S2, the effect of solvent systems on the formation of the target products

Solvent (S)	Vol (ml)	Products (precipitates)			Products (subject to filtration)		
		DHTZ-HM	DHTZ-TM	DHTZ-MB	DHTZ-HM	DHTZ-TM	DHTZ-MB
DMF	30	1,2,3,4	**2**	2,3,4	1,2,R	1,2,3	1,2,R
	15	2,3,4	2,3	-	1,2,3R	1,2,3R	-
	1	**p**	**P**	**p**	R	R	R
DMSO	30	1,2,3	1,2,3	2,3	1,2,3	1,2,3,4	2,3,4
	20	1,2,3,4	1,2,3	2,3	1,2,3	2,3	2,3
	10	2,3,4	2,3	-	1,2,R	2,3	2,3
	1	**p**	**P**	**P**	R	R	R
THF (poor yield)	30	1,2,R	2,R	2,R	R	R	R
	15	2,R	2,3,R	2,R	R	R	R
	1	2,3,4,R	2,R	2,3,R	R	R	R
THF:DMF 1:1	100	1,2	1,2,3	1,2	1,2	1,2,3	1,2
	50	1,2	2,3	1,2	1,2	2,3	1,2
	30	**2**	2,3	**2**	1,2	2,3	**2**
	15	2,3	2,3,p	2,3	2,3	R,2,3	2,3
	5	2,3,P	2,3,p	2,3	R,3	R,2,3	2,3
	1	**P**	**P**	**p**	R	R	R
THF:DMSO 1:1	30	1,2,3	2,3	2,3	1,2,3,R	2,3,R	2,3,R
	15	1,2,3	2,3	2,3	1,2,3,R	2,3,R	2,3,R
	1	**P**	**P**	**P**	R	R	R
MeCN (poor yield)	30	1,2,3,R	2,3,R	2,3,R	R	R	R
Pyridine (poor yield)	30	1,2,3,R	2,3,R	2,3,R	R	R	R
dioxane	30	R	R	R	R	R	R

Notes: the resulting products as determined by ESI-MS; N = 1, 2, 3, 4 denotes the number of repeating units in the cyclic products; If were remained, the mark "P" represents the formation of insoluble polymeric precipitates; mark "R" represents the reactant DHT was remained.

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It has been shown that DMF and DMSO are the most suitable solvents for macrocycle formation. However, DMSO would completely dissolve all the macrocycles, making it difficult to separate the cycles with different sizes. The solvents DMSO, DMF and their mixtures with tetrahydrofuran (THF) are suitable for preparation of the polymers. The yields from solvents such as THF, MeCN, pyridine and dioxane were very poor for both macrocycles and polymers, where the main precipitates were found to be the starting materials. In this case, two mixed solvents DMF/THF and DMSO/THF have been attempted, where THF is used as an antisolvent to help the precipitation of the products. It was found that for DHTZ-HM and DHTZ-MB, 30 ml of DMF/THF (mole ratio: 1/1) can be used to prepare the macrocycles with n=2 (C-DHTZ-HM and C-DHTZ-MB). Meanwhile, it was shown that the yield of DHTZ-TM with n=2 (C-DHTZ-TM) from 30 ml of DMF is the best. Here the electrospray ionization mass spectrometry (ESI-MS) technique has been used to determine the size of macrocycles.

Table S3, the local elemental distribution of the macromolecules from SEM/EDS analysis

P-DHTZ-HM	App	Intensity	Weight%	Weight%	Atomic%
C K	27.37	1.4150	42.24	1.12	47.00
N K	2.29	0.1248	40.04	1.49	38.20
O K	2.19	0.2698	17.72	0.84	14.80
Totals			100.00		
P-DHTZ-TM	(Uniform Matrix)				
C K	11.66	1.4645	52.48	4.10	57.58
N K	0.42	0.0981	28.01	5.40	26.35
O K	0.87	0.2932	19.50	2.21	16.07
Totals			100.00		
P-DHTZ-MB	(Uniform Matrix)				
C K	11.95	1.5493	69.51	9.10	74.53
N K	0.07	0.0724	8.14	11.82	7.48
O K	0.84	0.3402	22.35	3.40	17.99
Totals			100.00		
P-DHTZ-MB	(BALL STRUCTURE)				
C K	20.62	1.4263	43.11	1.71	47.86
N K	1.63	0.1221	39.82	2.24	37.91
O K	1.54	0.2681	17.08	1.25	14.23
Totals			100.00		
C-DHTZ-HM	(Uniform Matrix)				
C K	12.50	1.3834	9.04	0.18	47.52
N K	1.06	0.1225	8.68	0.74	39.12
O K	0.81	0.2632	3.06	0.26	12.07
Totals			100.00		
C-DHTZ-TM	(Uniform Matrix)				
C K	10.01	1.3344	7.50	0.17	38.40
N K	1.61	0.1499	10.72	0.71	47.08
O K	0.93	0.2540	3.65	0.29	14.03
Totals			100.00		
C-DHTZ-MB	(Uniform Matrix)				
C K	12.77	1.3849	9.23	0.18	52.21
N K	0.74	0.1096	6.71	0.79	32.55
O K	0.99	0.2797	3.54	0.25	15.04
Totals			100.00		

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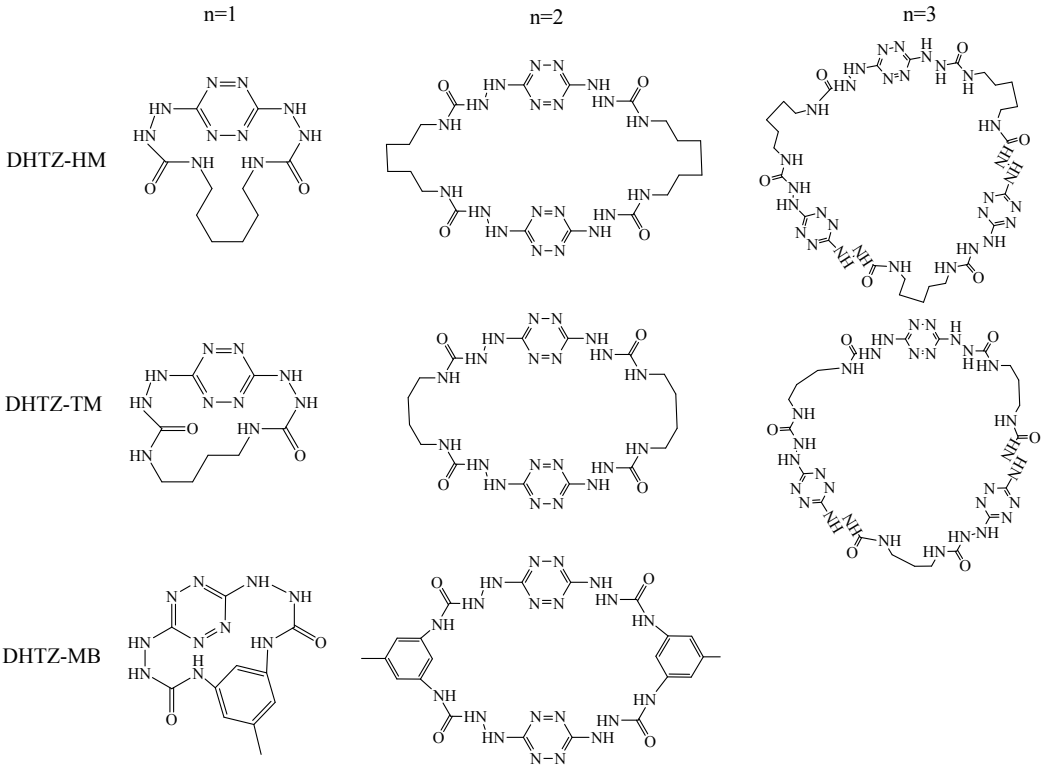
Table S4. Solubility of synthesized macromolecules in DMSO and in DMF (at 30 °C).

Compound	Solubility in DMSO (mg/ml)	Solubility in DMF (mg/ml)
C-DHTZ-HM	7.1	1.9
C-DHTZ-TM	4.5	3.3
C-DHTZ-MB	10.0	2.4



Scheme S1, the cycles of DHTZ-HM, DHTZ-TM and DHTZ-MB in various sizes where "n" represents the number of times for using the precursors.

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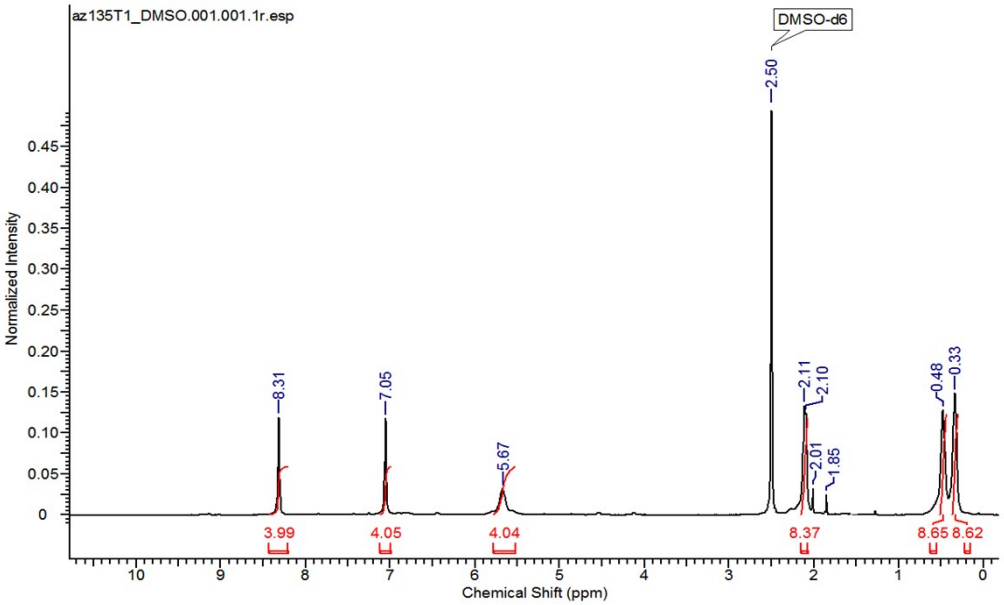

Figure S1, 1H NMR of C-DHTZ-HM in DMSO-d[6]

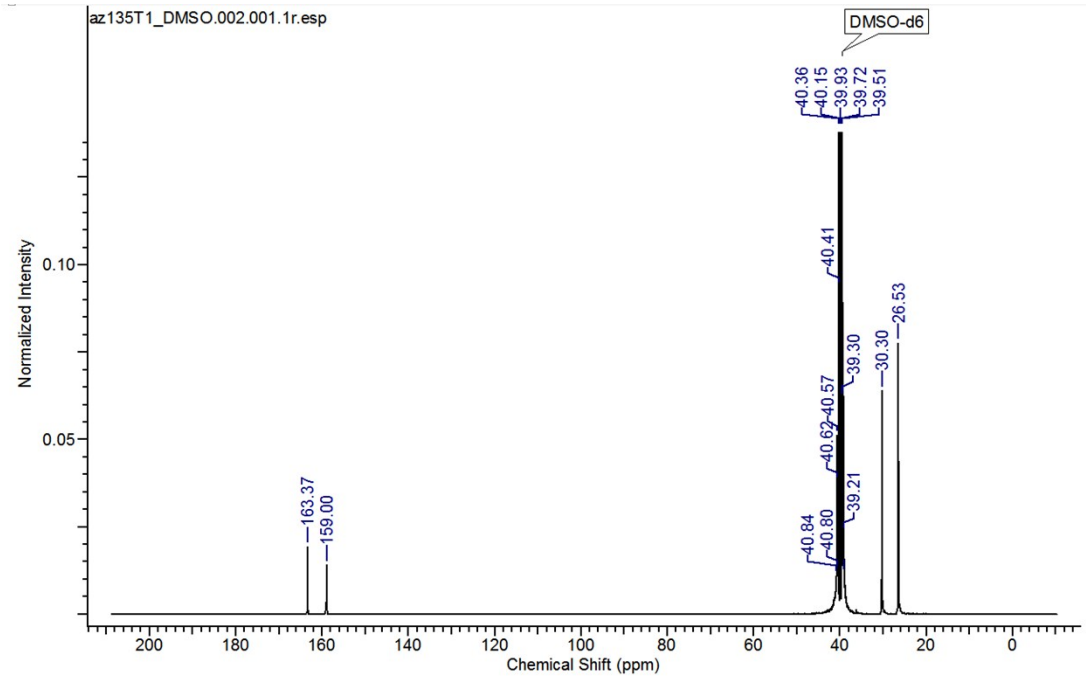

Figure S2, 13C NMR of C-DHTZ-HM in DMSO-d[6]

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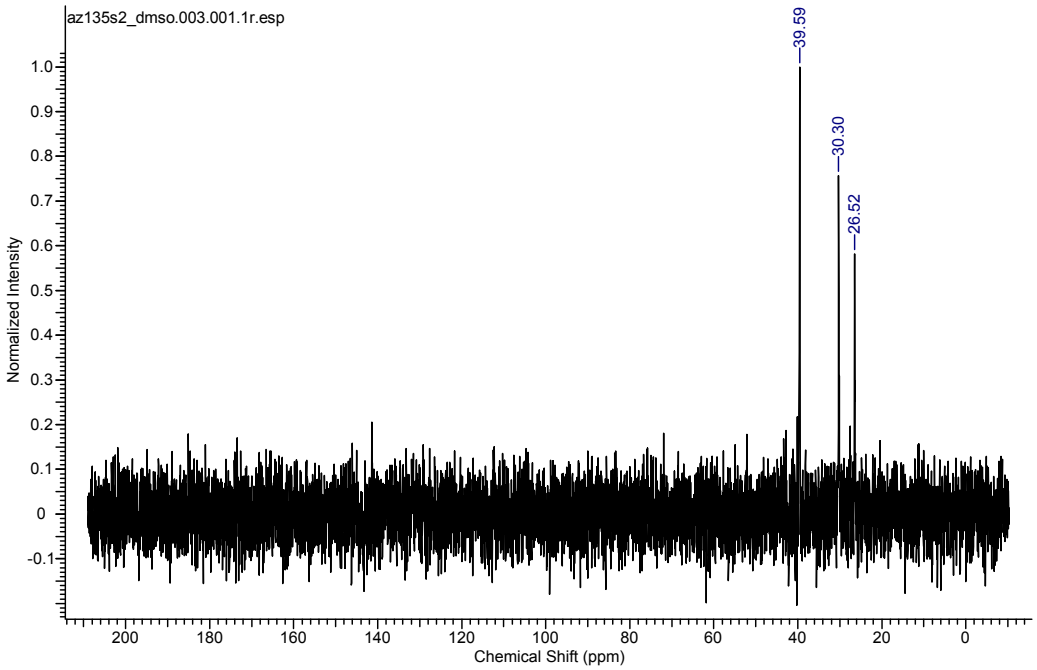
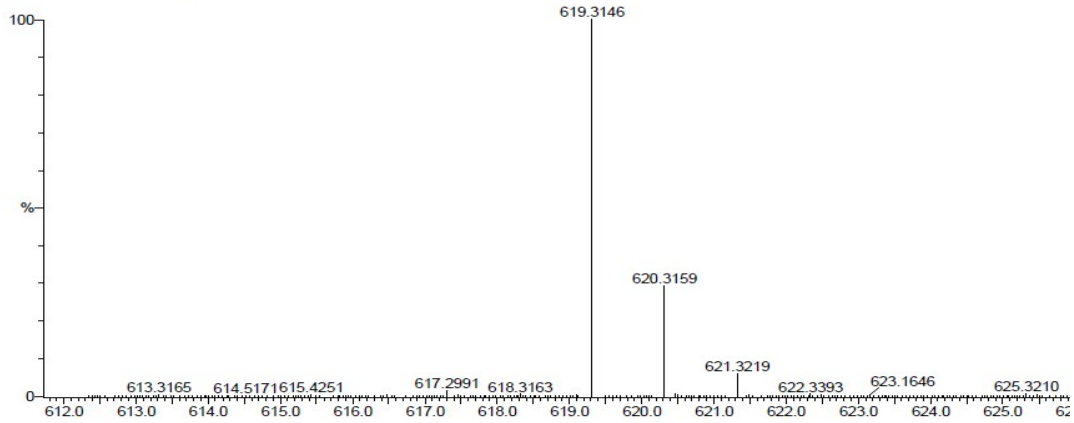


Figure S3, DEPT NMR of C-DHTZ-HM in DMSO-d^6

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
315 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 10-30 H: 30-50 N: 10-30 O: 0-10

AZ135T5
Gozin371b 30 (1.155) Cm (19:31)



Minimum:				-1.5						
Maximum:		5.0	5.0	50.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
619.3146	619.3150	-0.4	-0.6	13.5	152.8	1.5	C20	H35	N20	O4
	619.3137	0.9	1.5	8.5	152.5	1.2	C19	H39	N16	O8
	619.3164	-1.8	-2.9	7.5	152.1	0.8	C23	H43	N10	O10
	619.3164	-1.8	-2.9	18.5	156.1	4.8	C21	H31	N24	
	619.3123	2.3	3.7	14.5	157.7	6.4	C16	H31	N26	O2

Figure S4, HRMS of C-DHTZ-HM in DMSO-d^6

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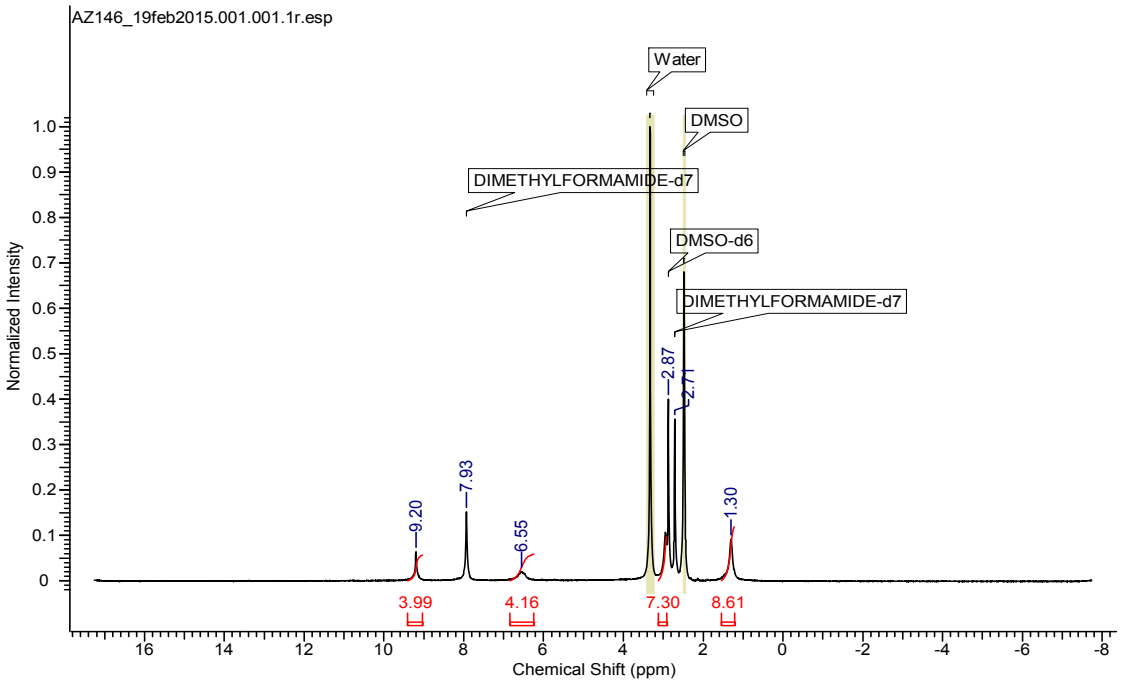

Figure S5, 1H NMR of C-DHTZ-TM in DMSO-d^6

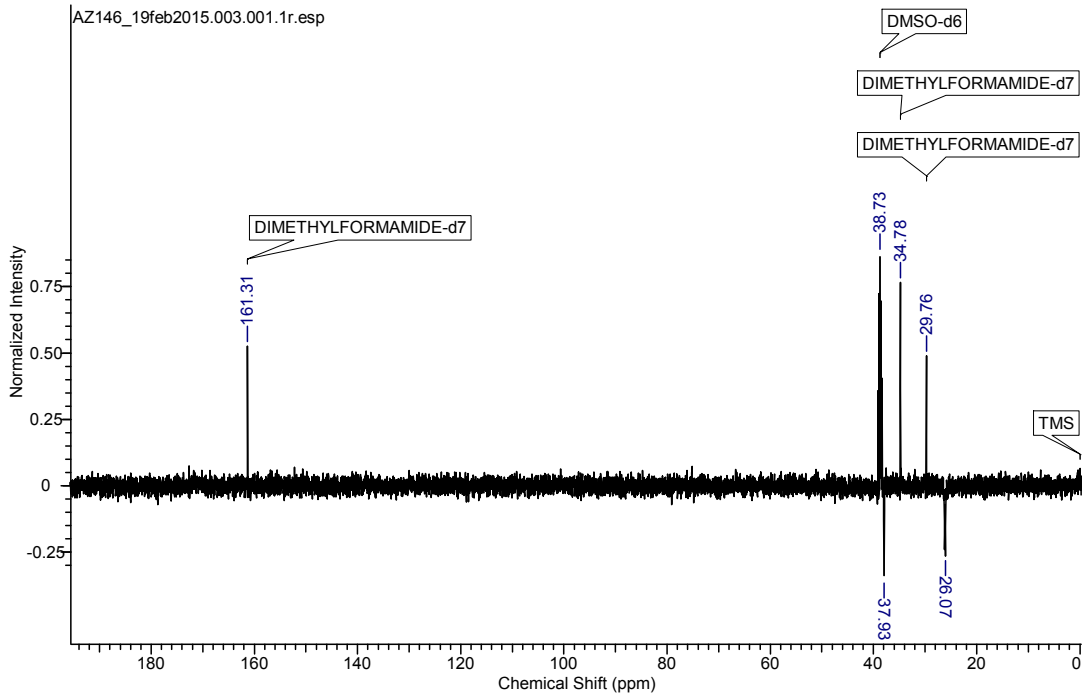

Figure S6, DEPT NMR of C-DHTZ-TM in DMSO-d^6

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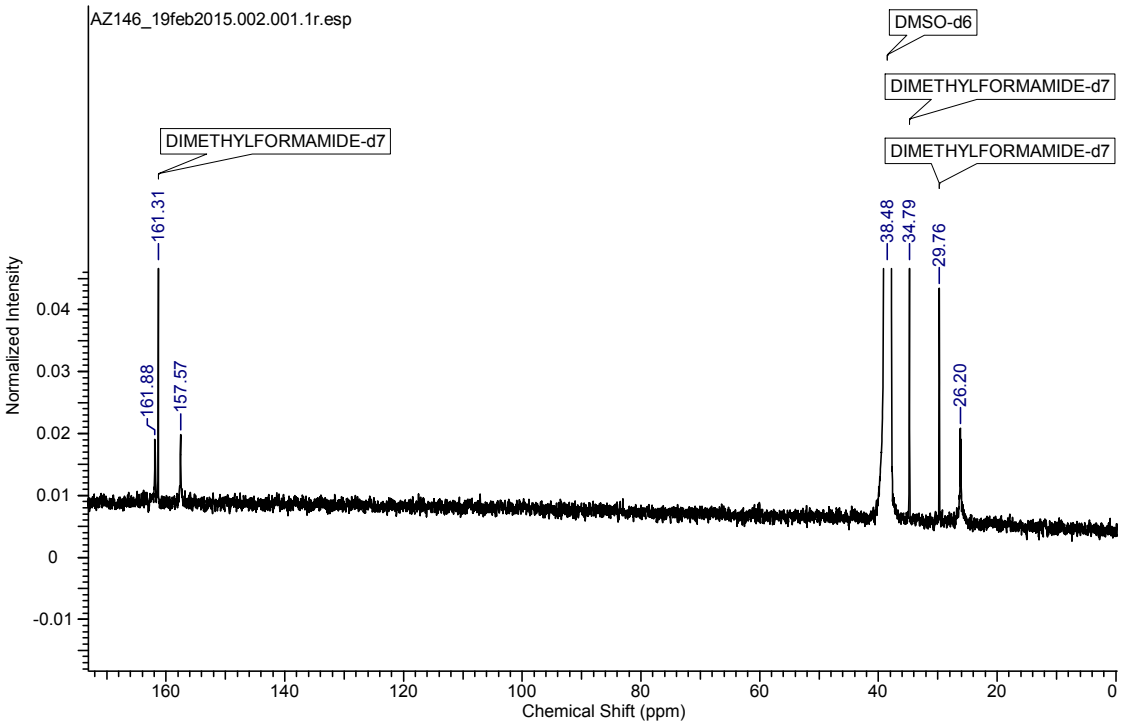
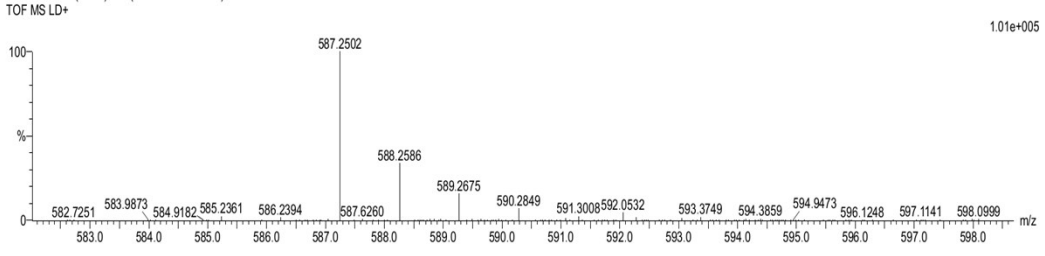


Figure S7, 13C NMR of C-DHTZ-TM in DMSO-d6

Elemental Composition Report

Single Mass Analysis
Tolerance = 0.5 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
827 formula(e) evaluated with 2 results within limits (up to 5 best isotopic matches for each mass)
Elements Used:
C: 10-20 H: 20-40 N: 10-30 O: 0-20 Na: 0-1
GOZIN373 21 (1.067) Cm (19:28-34:41x2.000)
TOF MS LD+



Minimum:				-1.5			
Maximum:		5.0	0.5	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
587.2502	587.2500	0.2	0.3	12.5	211.4	0.9	C16 H28 N20 O4 Na
	587.2500	0.2	0.3	7.0	211.0	0.5	C17 H34 N13 O9 Na

Figure S8, HRMS of C-DHTZ-TM in DMSO-d6

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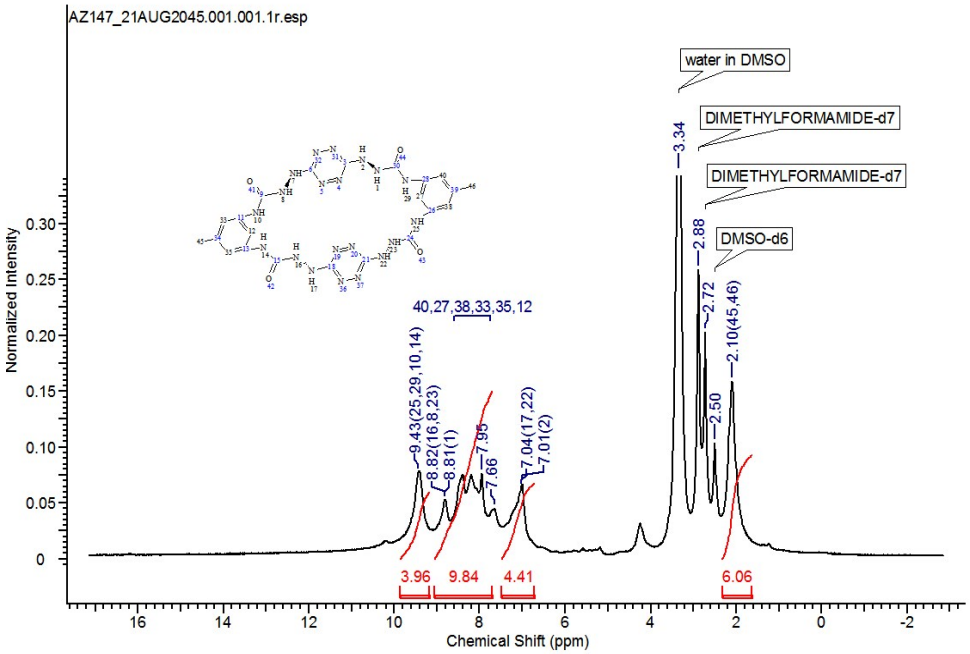

Figure S9, ^{1}H NMR of C-DHTZ-MB in DMSO-d^{6}

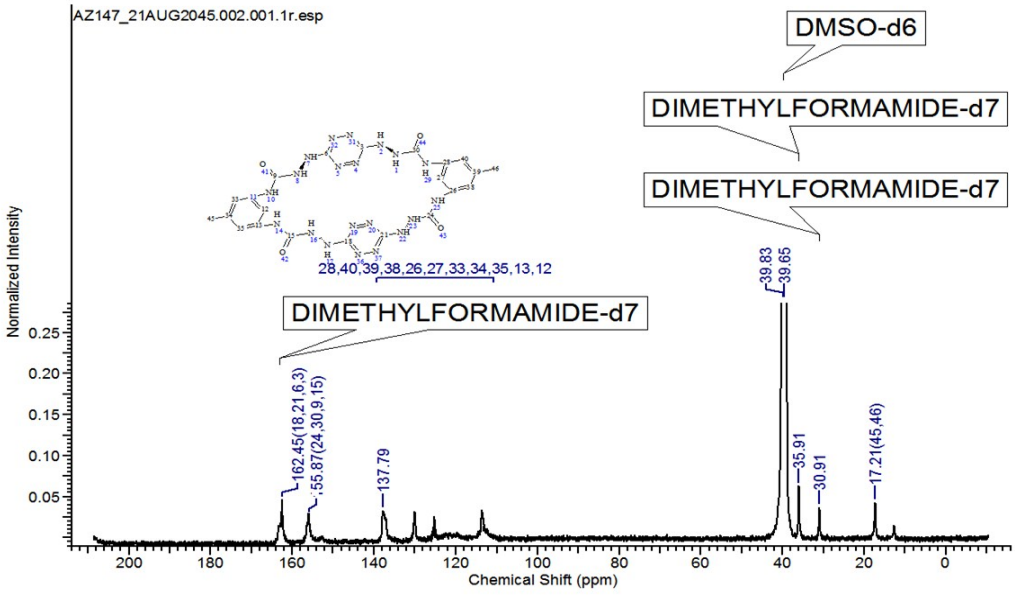

Figure S10, ^{13}C NMR of C-DHTZ-MB in DMSO-d^{6}

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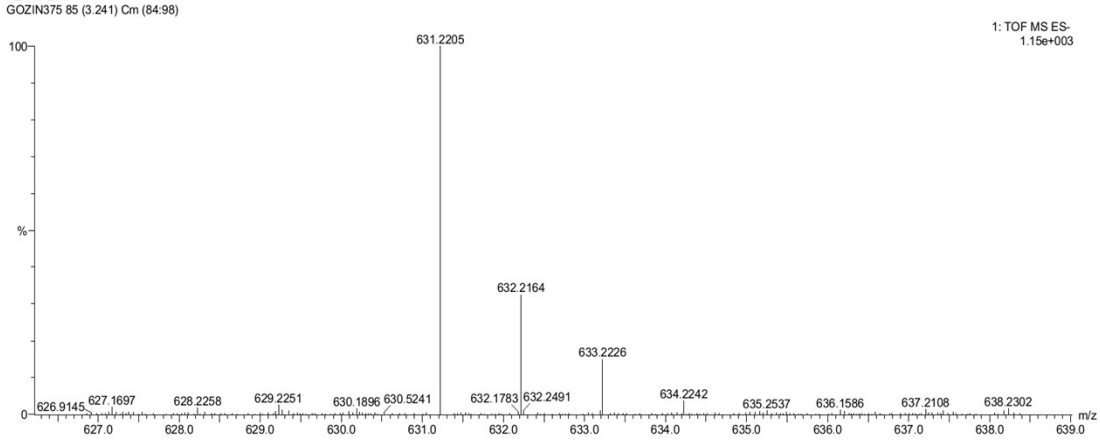
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
166 formula(e) evaluated with 2 results within limits (up to 5 best isotopic matches for each mass)
Elements Used:
C: 15-30 H: 20-30 N: 10-30 O: 0-10
AZ-147-2
GOZIN375 85 (3.241) Cm (84:98)



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
631.2205	631.2198	0.7	1.1	16.5	97.9	0.5	C21 H27 N16 O8
	631.2211	-0.6	-1.0	21.5	98.2	0.9	C22 H23 N20 O4

Figure S11, HRMS of C-DHTZ-MB in DMSO-d6

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