Electronic Supplementary Material (ESI) for Chemical Science.

Electronic supporting information

Extending accessible heptazine chemistry; 2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine, a new highly soluble heptazine derivative with exchangeable groups, and examples of new derived heptazines with their physical chemistry.

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1. Synthesis

All chemicals were of reagent grade and used without further purification. All reactions were monitored by thin-layer chromatography (TLC) using a Merck TCL silica gel 60 F254. NMR spectra were recorded on a JEOL JMS ECS 400 MHz spectrometer (100 MHz for ^{13}C). High resolution mass spectroscopy was performed using the CNRS Imaging platform.

Synthetic procedures.

2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (**1**)

About 20 g of trishydrazinoheptazine are prepared according to Kroke[1] (quickly reminded, it involves heating melem finely ground powder for 24 h at 140°C in an autoclave with a large excess of pure hydrazine hydrate (Acros chemicals); however, as mentioned in the main article text, we did not perform the purification steps and used the crude product). The crude product is then filtered off, rinced three times with distilled water, and let dry two days in a closed dessicator with phosphoric anhydride before being used without further purification.

Then 2 g (7.6 mmol) of 2,5,8-trihydrazinoheptazine powder are introduced in a 80 mL agate planetary milling bowl with 2.7 g (34.2 mmol, 4.5 eq.) of 3,5-heptanedione c.a. 0.5 g of p-toluenesulfonic acid monohydrate (3 mmol, 0.4 eq) and 2 g of silica powder (40-70 nm) along with 15 agate 1 cm diameter milling balls. The milling bowl is fitted to a planetary mixer (Fritsch, Pulverisette, model 6 classic) and operated 8 minutes at 500 rpm. The resulting paste extracted 3 times with dichloromethane (DCM, ca 50 mL each time). The fractions are gathered, the silica initially in the mixture is filtered off, and the solvent is evaporated. The product is purified on a flash chromatography set up (prepacked 80 g silica column, eluent petroleum ether (PE)/ethyl acetate (EA) with a gradient over 30 mn from pure PE to pure EA (for perfect elimination of excess ketone and traces of ketone coupling products). In a typical experiment about 1.2 g (31 % yield) are produced (white powder, bluish white fluorescence). Please note that the yield is calculated from the amount of trihydrazinoheptazine which was not purified at the start.

^{1}H NMR ($CDCl_3$, 400 MHz): 1.29 (6 H, 2 t, 2 x $-CH_3$, J = 7.2 Hz, J = 8 Hz), 2.73 (2 H, $-CH_2$, q, J = 8 Hz), 3,27 (2 H, $-CH_2$, q, J = 7.2 Hz), 6.2 (1 H, -CH, s), in ppm.

^{13}C NMR (CDCl3, 100 MHz): 12.7, 13.0, 22.1, 23.7, 110.1, 153.0, 158.6, 161.0, 163.2, in ppm.

HRMS calculated for $C_{27}H_{33}N_{13}$ ($M + H^+$): 540.3015, found: 540.3063

2,5,8-trimorpholino-heptazine (**2a**)

2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (1 g, 1.8 mmol) is dissolved in 50 mL acetonitrile. 0.52 g (6 mmol, 3.3 eq.) of morpholine (Acros Chemicals) are added with the help of a syringe. The reaction starts immediately, then slows down; after 5 mn, the mixture is brought to reflux for 2 hours. The solvent is then evaporated, and the crude product is purified by a flash chromatography (40 g silica column, pure EA) which allows to separate 550 mg of 2,5,8-trimorpholinoheptazine as a white powder with a violin fluorescence (71 % yield).

^{1}H NMR ($CDCl_3$, 400 MHz): 3.71 (4 H, t, -CH_2N, J = 4.8 Hz), 3.94 (4 H, -CH_2O, t, J = 4.8 Hz),in ppm.

^{13}C NMR (CDCl3, 100 MHz): 44.7, 66.9, 155.2, 162.1, in ppm.

HRMS calculated for $C_{18}H_{24}N_{10}O_2$ (M + H$^+$): 429.2066, found: 429.2116

2,5,8-tri(piperidin-1-yl)-heptazine (**2b**)

2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (405 mg, 0.75 mmol) is dissolved in 10 mL acetonitrile. 211 mg (2.5 mmol, 3.3 eq.) of piperidine are added with the help of a syringe. The mixture is heated at 60°C for 3 hours. The solvent is then evaporated and the crude product is recrystallized in ethanol to give 232 mg of 2,5,8-tri(piperidin-1-yl)-heptazine as a white powder with a violin fluorescence (73 % yield).

^{1}H NMR ($CDCl_3$, 400 MHz): 3.87 (4 H, t), 1.55-1.75 (6 H, m), in ppm.

^{13}C NMR (CDCl3, 100 MHz): 24.6, 26.2, 44.2, 155.2, 161.2, in ppm.

HRMS calculated for $C_{21}H_{30}N_{10}$ (M + H$^+$): 423.2733, found: 423.2731

2,5,8-tri(pyrrolidin-1-yl)-heptazine (**2c**)

2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (405 mg, 0.75 mmol) is dissolved in 10 mL acetonitrile. 176 mg (2.5 mmol, 3.3 eq.) of pyrrolidine are added with the help of a syringe. The mixture is heated at 60°C for 3 hours. The solvent is then evaporated and the crude product is recrystallized in ethanol to give 180 mg of 2,5,8-tri(pyrrolidin-1-yl)-heptazine as a white powder with a violin fluorescence (63 % yield).

^{1}H NMR ($CDCl_3$, 400 MHz): 3.72 (4 H, q), 1.93 (4 H, q), in ppm.

^{13}C NMR (CDCl3, 100 MHz): 25.2, 47.4, 154.7, 160.9, in ppm.

HRMS calculated for $C_{18}H_{24}N_{10}$ (M + H$^+$): 381.2264, found: 381.2273

2,5,8-tris(2-ethylhexyl-1-amine)-heptazine (**2d**)

2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (405 mg, 0.75 mmol) is dissolved in 10 mL acetonitrile. 320 mg (2.5 mmol, 3.3 eq.) of 2-ethylhexyl-1-amine are added with the help of a syringe. The mixture is brought to reflux for 3 hours. The solvent is then evaporated and the crude product is recrystallized in ethanol to give 205 mg of 2,5,8-tris(2-ethylhexyl-1amine)-heptazine as a white powder with a violin fluorescence (49 % yield).

^{1}H NMR ($CDCl_3$, 400 MHz): 0.89 (6 H, 2 x –CH_3, 2 t), 1.28 (6 H, 3 x -CH2-, m), 1.34 (2 H, -CH2-, dq), 1.51 (1 H, -CH-, m), 3.39-3.49 (2 H, -CH2-NH-, m), 5,42-5,48 (1 H, -NH-, m) in ppm.

^{13}C NMR (CDCl3, 100 MHz): 10.9, 14.2, 23.1, 24.1, 28.8, 30.9, 39.2, 44.2, 155.4, 164.1 in ppm.

HRMS calculated for $C_{30}H_{54}N_{10}$ (M + H$^+$): 555.4611, found: 555.4637

*2,5,8-tris((4-butylphenyl)thio)-heptazine (**3a**)*

2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (1 g, 1.8 mmol) is dissolved in 50 mL acetonitrile. 1.06 g (5.95 mmol, 3.3 eq.) of 4-butylphenylthiol (Acros chemicals) are added in one portion. The mixture is brought to reflux overnight. The acetonitrile is then evaporated, and the reactional mixture subjected to flash chromatography (80 g silica column, pure EA) which allows to separate 950 mg of 2,5,8-tris((4-butylphenyl)thio)-heptazine as a white powder with a white-violin fluorescence (75 % yield).

^{1}H NMR ($CDCl_3$, 400 MHz): 0.94 (3 H, t, -CH_3), 1.38 (2 H, -CH_2-, m), 1.59 (2 H, -CH_2-, m), 2.62 (2 H, Ph-CH_2-, t), 7.21 (2 H, Ph ring, d, J = 8 Hz), 7.39 (2 H, Ph ring, d, J = 8 Hz) in ppm.

^{13}C NMR (CDCl3, 100 MHz): 14.1, 22.5, 33.4, 35.0, 123.2, 129.6, 134.9, 145.6, 153.1 in ppm.

2,5,8-tris(phenylthio)-heptazine (**3b**)

2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (500 mg, 0.93 mmol) is dissolved in 24 mL acetonitrile. 462 mg (4.19 mmol, 4.5 eq) of thiophenol (Acros Chemicals) are added with the help of a syringe, then 512 mg DMAP (4.5 eq) are added to the mixture which is brought to reflux for 2 hours. The solvent is then evaporated, and the crude product is purified by a flash chromatography (80 g silica column, PE/DCM (20/80)) which allows to separate 100 mg of 2,5,8-tris(phenylthio)heptazine as a white powder with a yellow fluorescence (22 % yield).

^{1}H NMR ($CDCl_3$, 300 MHz): 7.37-7.44 (3 H, m), 7.50 (2 H, dd, J = 7.4, 1.9 Hz) in ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): 126.4, 129.4, 130.3, 135.0, 153.1, 188.3 in ppm.

HRMS calculated for $C_{27}H_{21}N_7S_3$ (M + H$^+$): 498.0629, found: 498.0643.

2,5,8-tris(benzylthio)-heptazine (**3c**)

2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (300 mg, 0.56 mmol) is dissolved in 15 mL acetonitrile. 230 mg (1.85 mmol, 3.3 eq) of benzylthiol (Acros Chemicals) are added with the help of a syringe, then 0.24 mL of 2,4,6-Collidine (3.3 eq) are added to the mixture which is brought to reflux for 2 hours. The solvent is then evaporated, and the crude product is purified by a flash chromatography (80 g silica column, PE 70/EtOAc 30) which allows to separate 205 mg of 2,5,8-tris(benzylthio)-heptazine as a yellow powder with a yellow fluorescence (68 % yield).

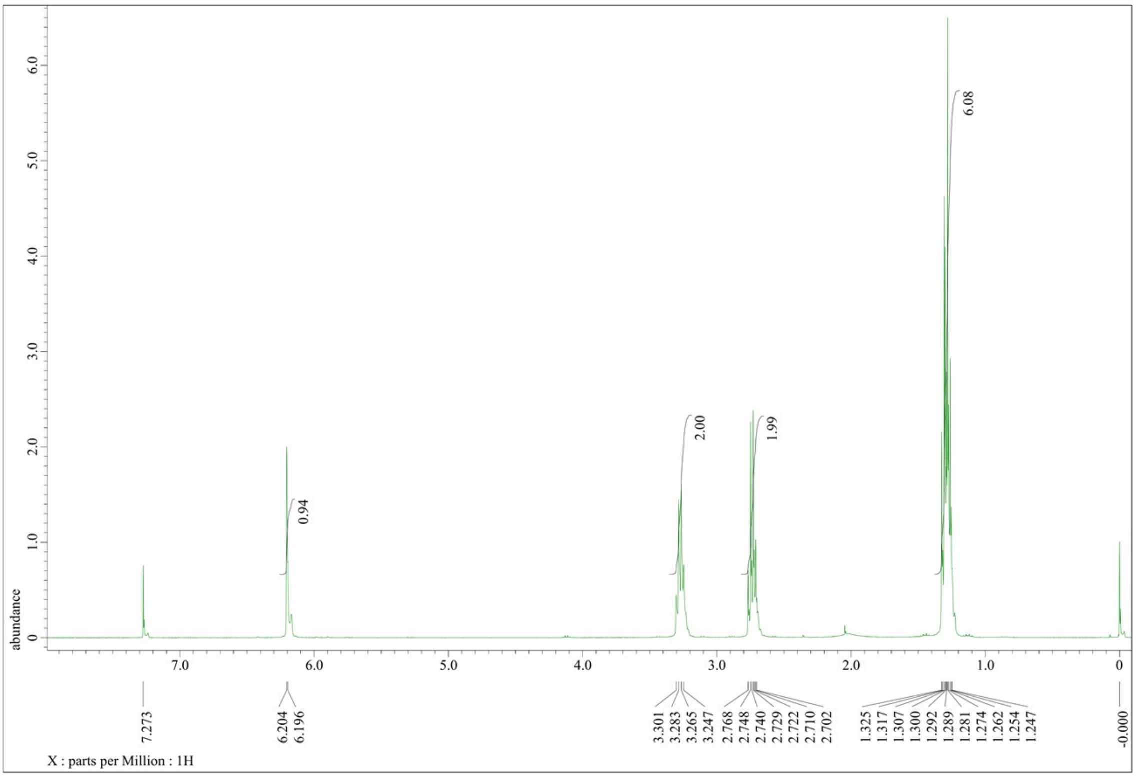
^{1}H NMR ($CDCl_3$, 300 MHz): 4.44 (6 H, s, $-CH_2$), 7.28-7.41 (15 H, m) in ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): 36.1, 127.8, 128.8, 129.2, 135.5, 152.5, 187.6 in ppm.

HRMS calculated for $C_{27}H_{21}N_7S_3$ ($M + H^+$): 540.1099, found: 540.1096.

NMR spectra

Figure S1: 2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (**1**):



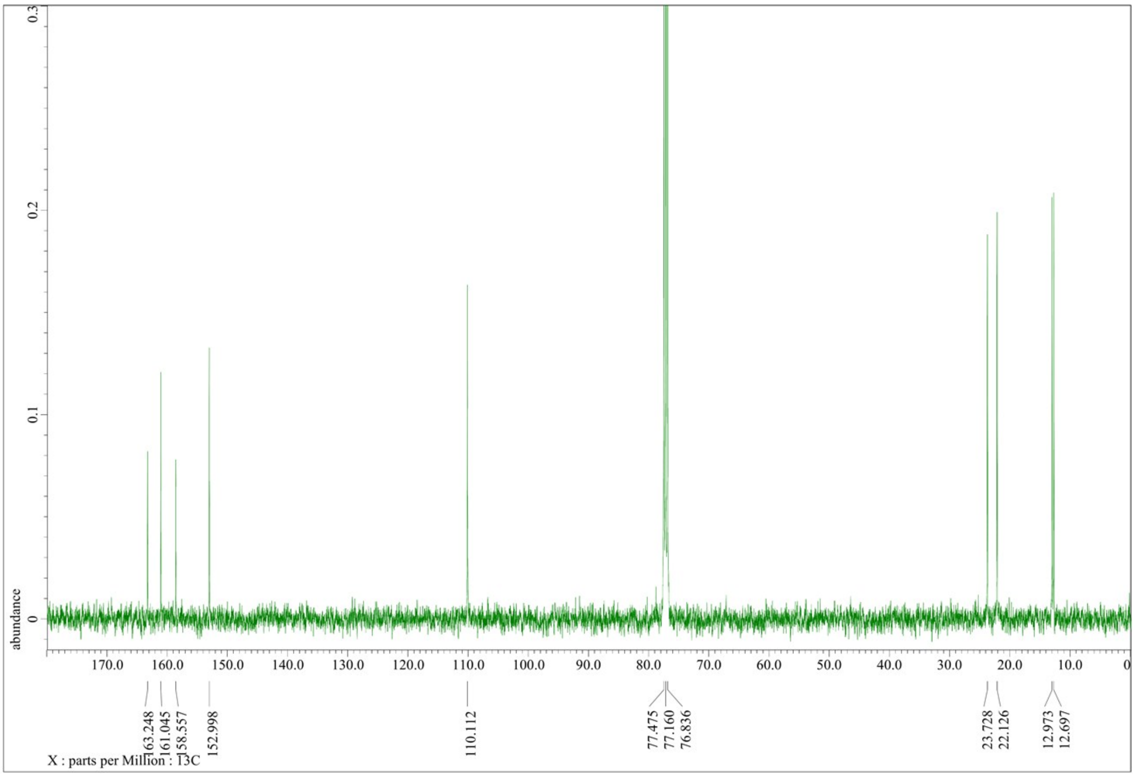


Figure S2: 2,5,8-trimorpholino-heptazine (**2a**)

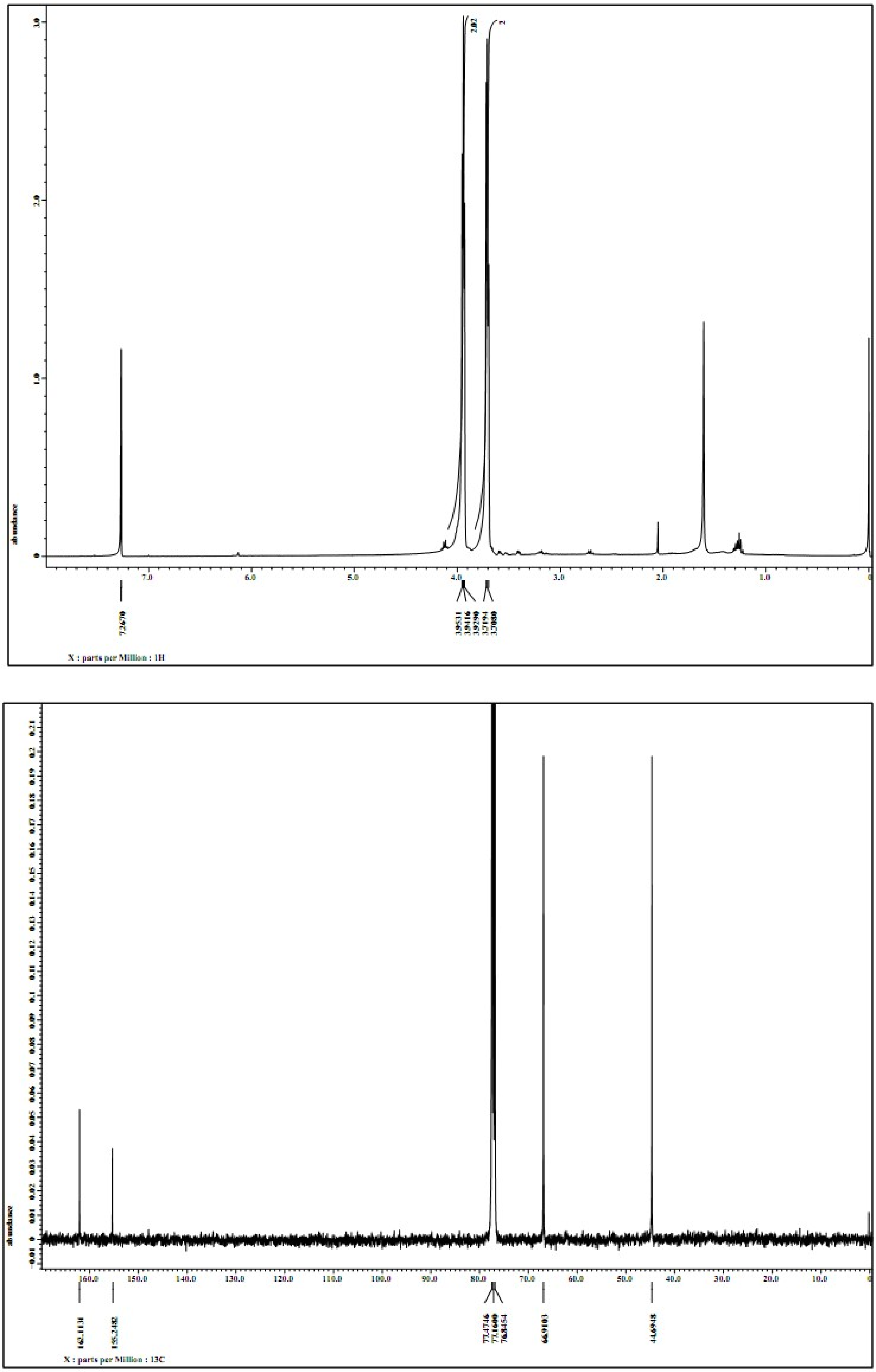
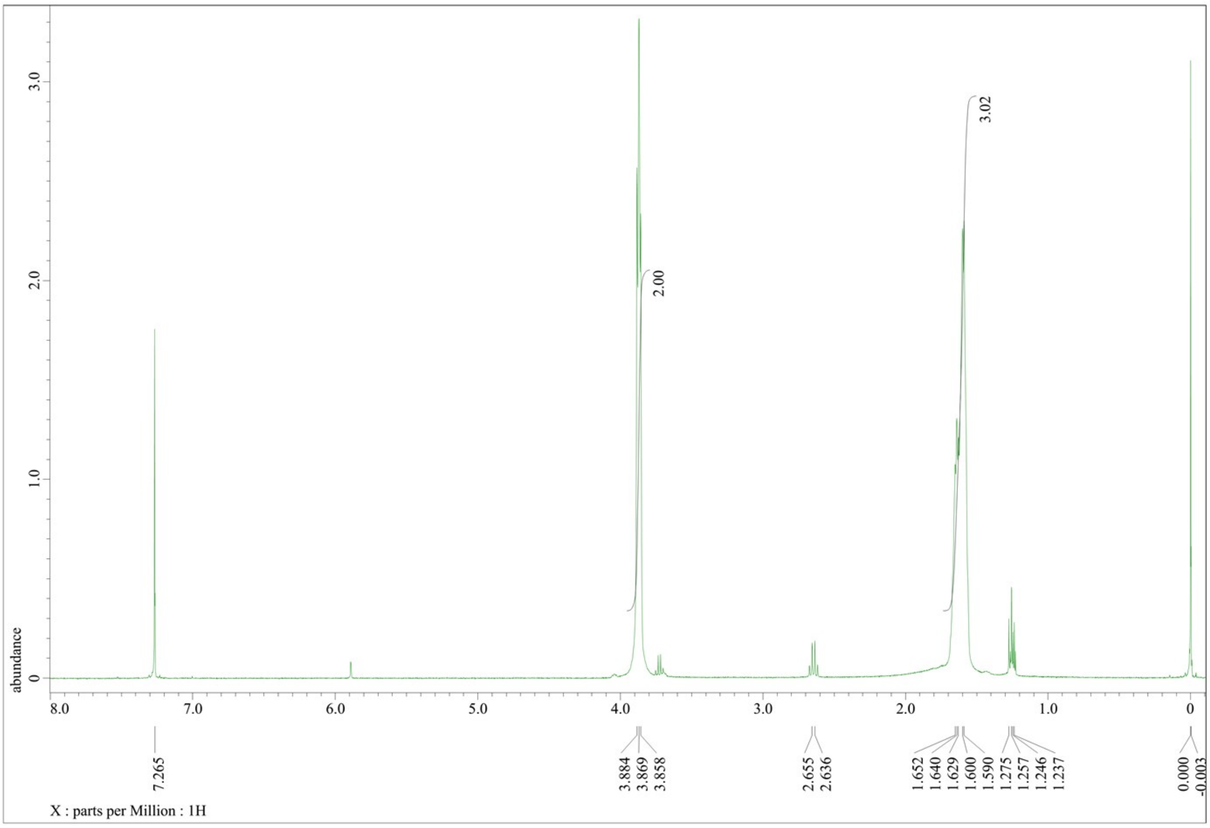


Figure S3: 2,5,8-tri(piperidin-1-yl)-heptazine (**2b**)



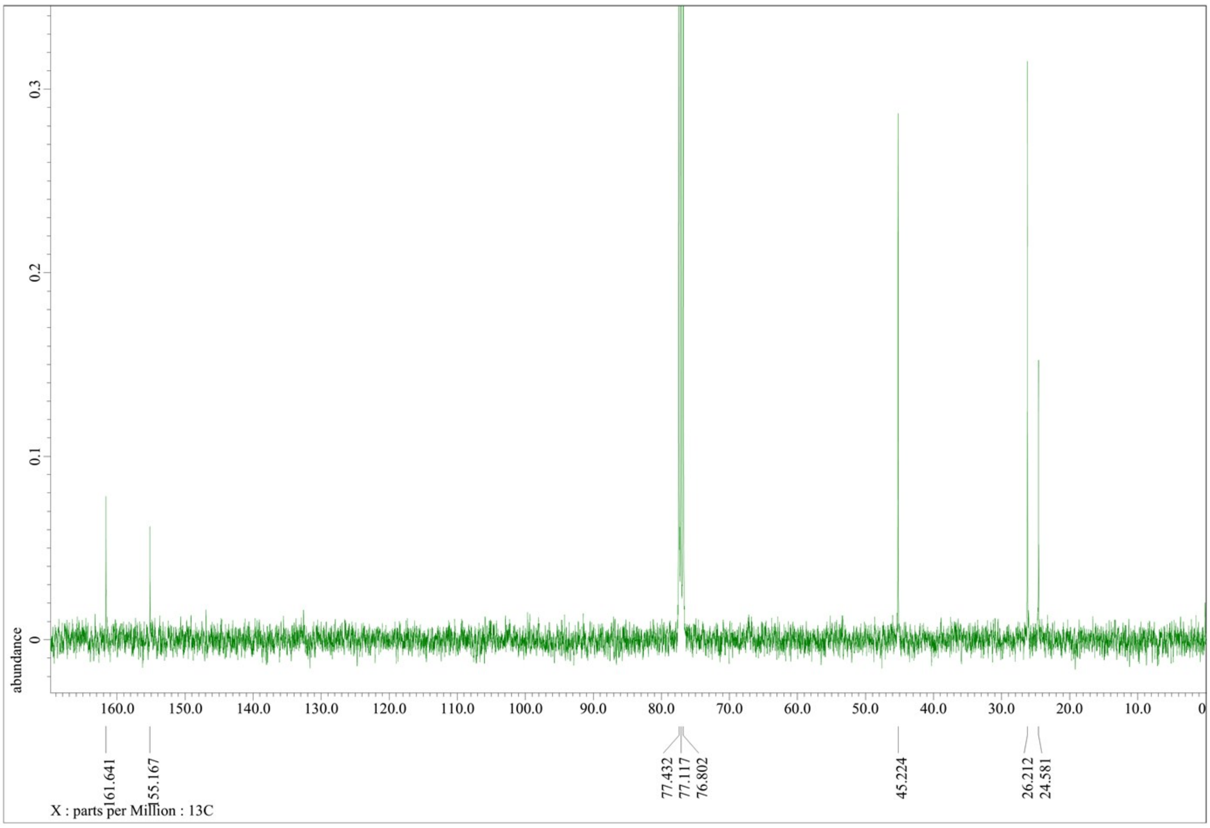
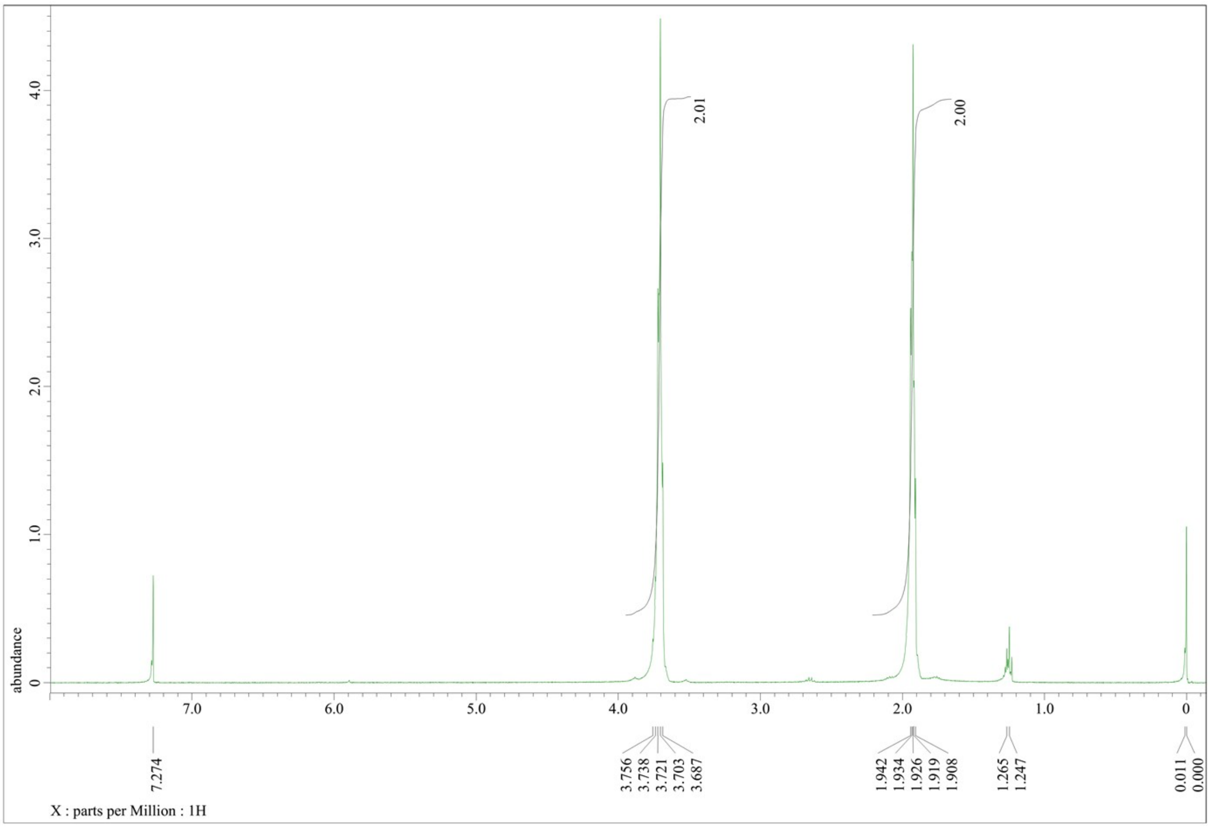


Figure S4: 2,5,8-tri(pyrrolidin-1-yl)-heptazine (**2c**)



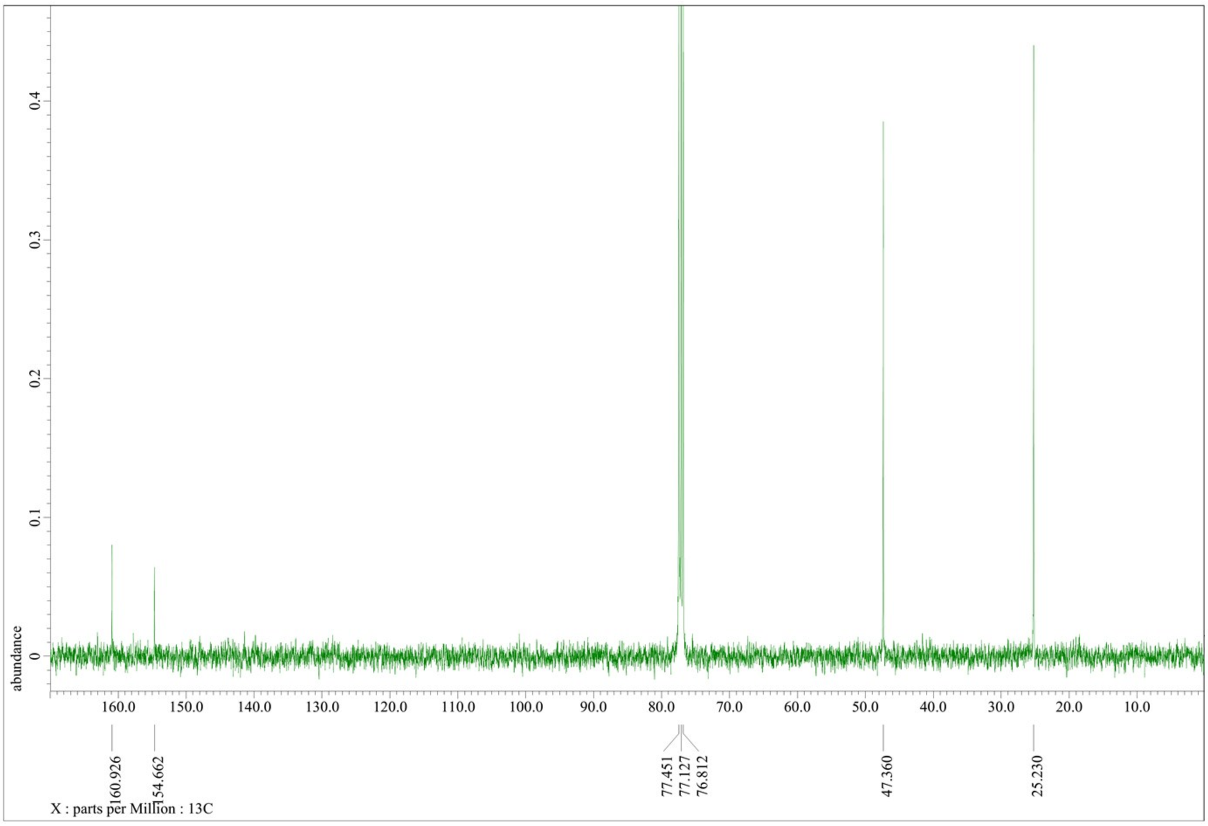
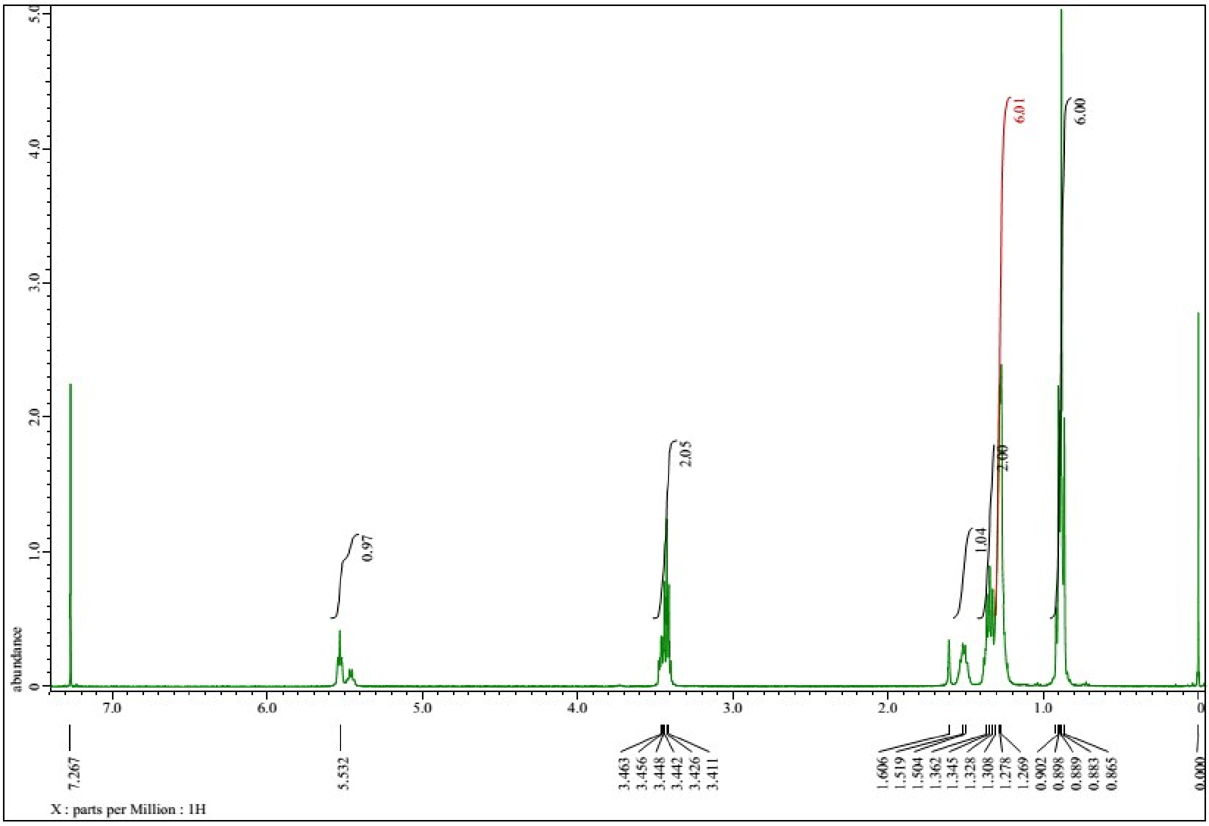


Figure S5 : 2,5,8-tris(2-ethylhexyl-1-amine)-heptazine (**2d**)



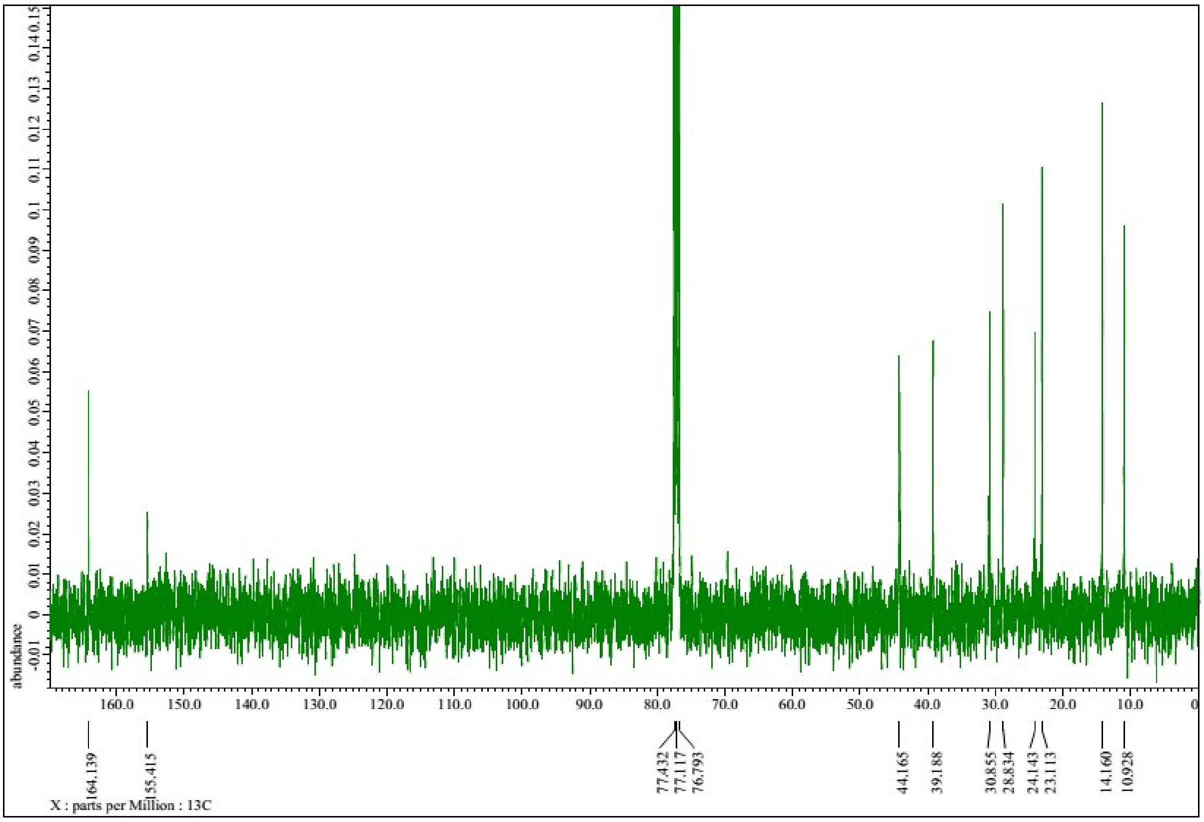


Figure S6: 2,5,8-tris((4-butylphenyl)thio)-heptazine (**3a)**

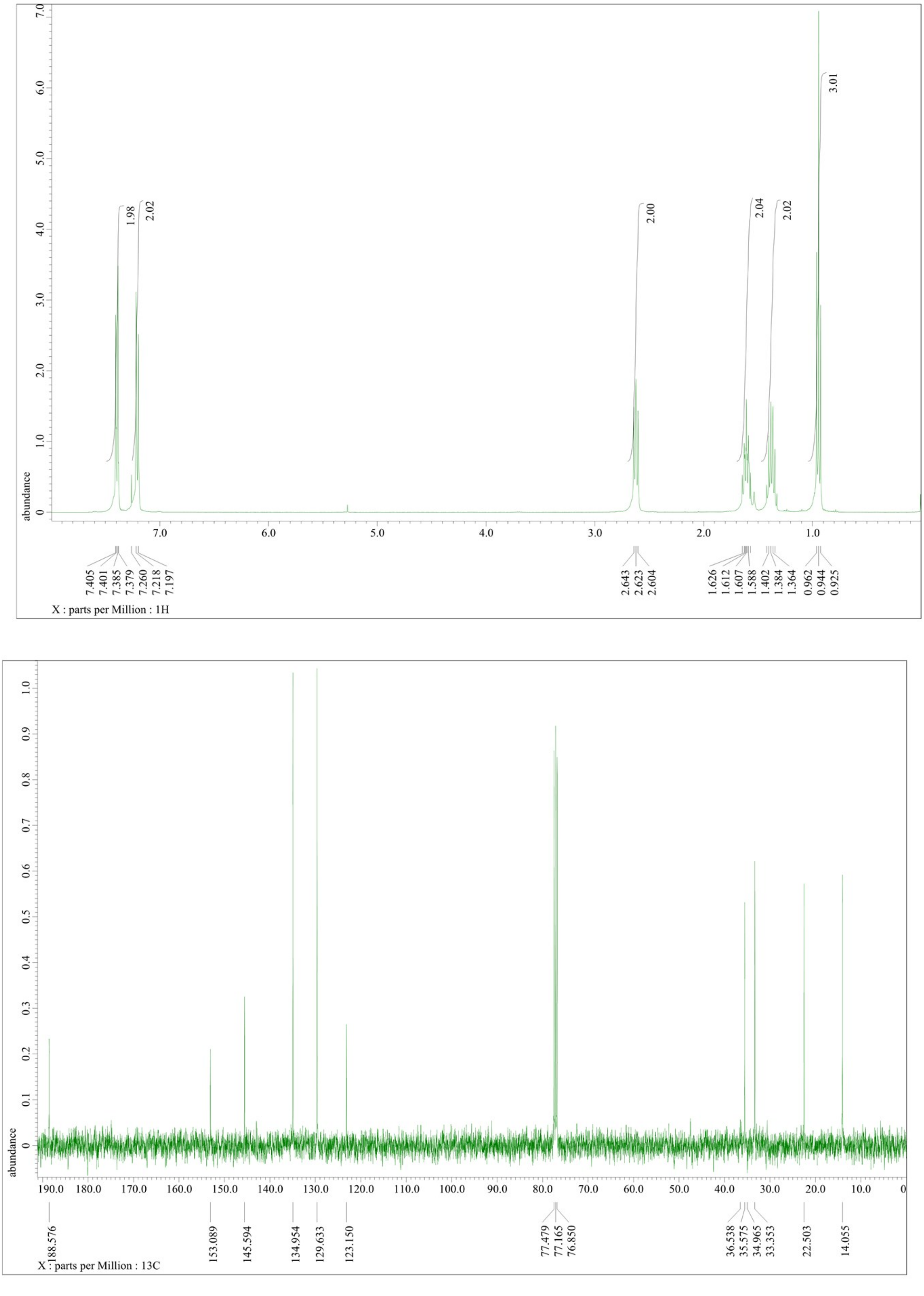


Figure S7: 2,5,8-tris(phenylthio)-heptazine (**3b**)

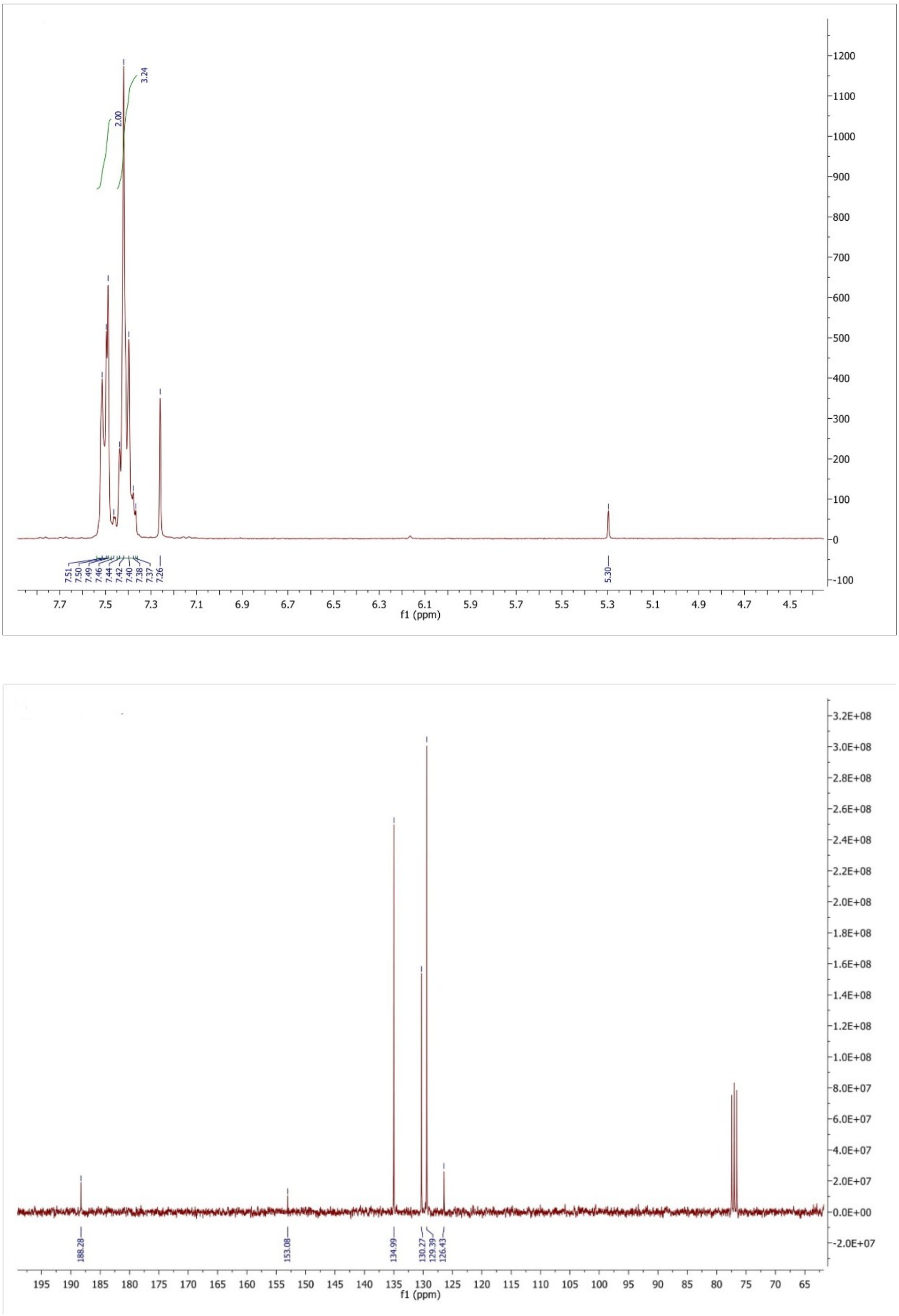
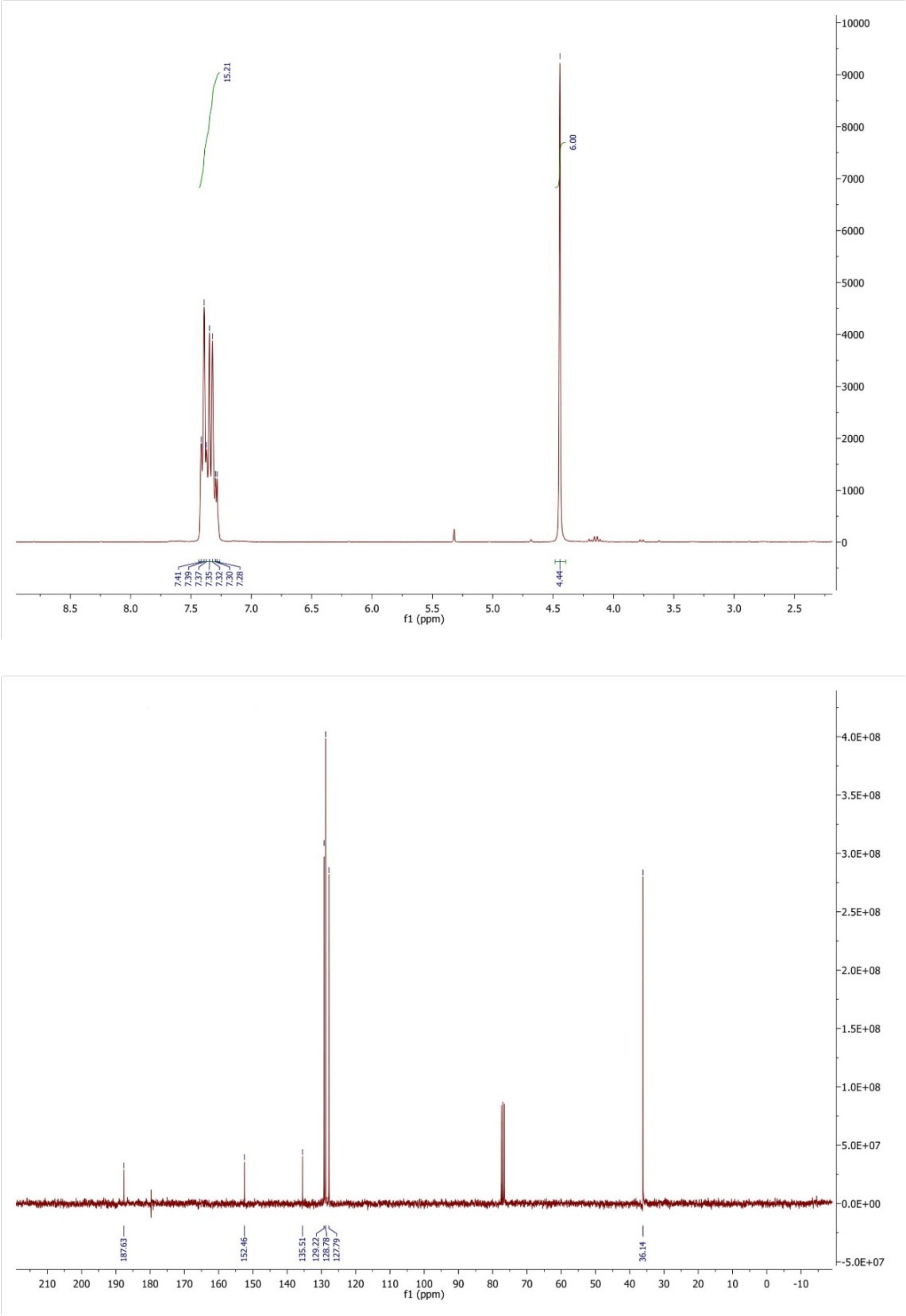
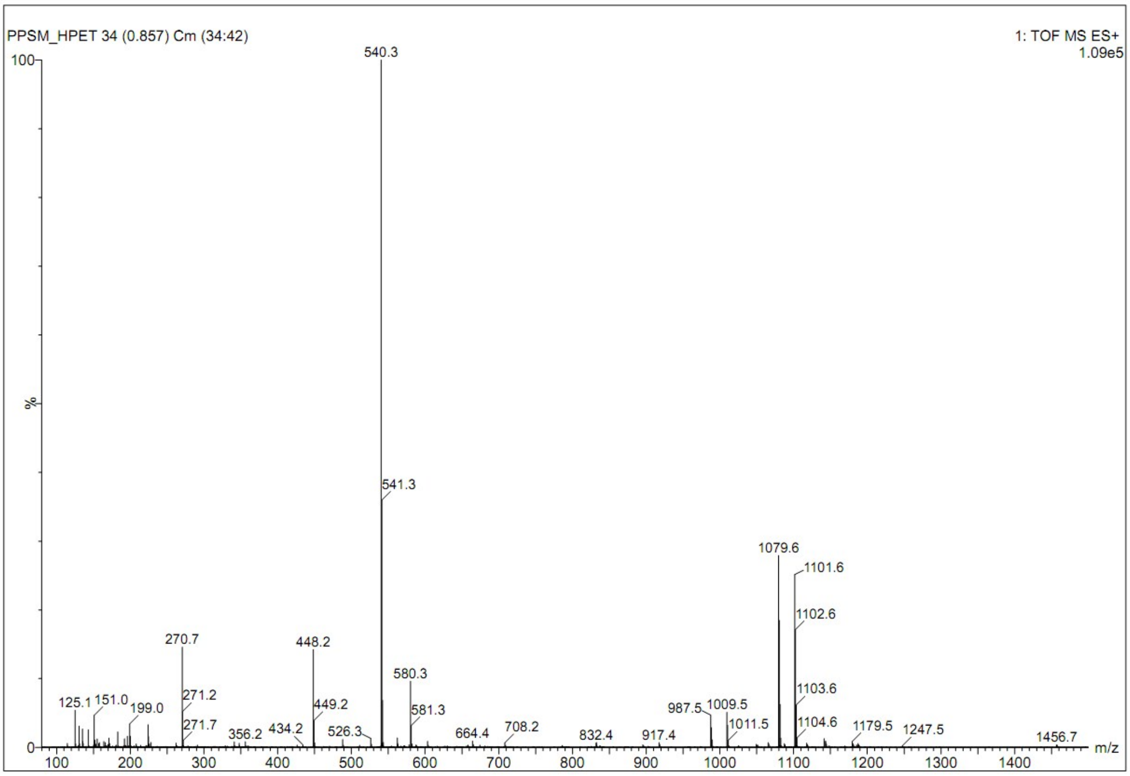


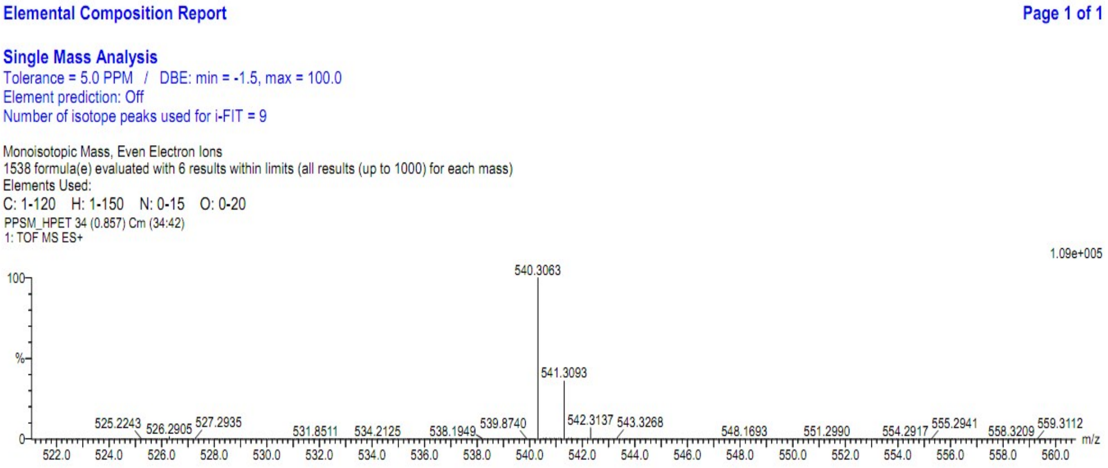
Figure S8: 2,5,8-tris(benzylthio)-heptazine (**3c**)



Mass Spectrometry

Figure S9: 2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (**1**)



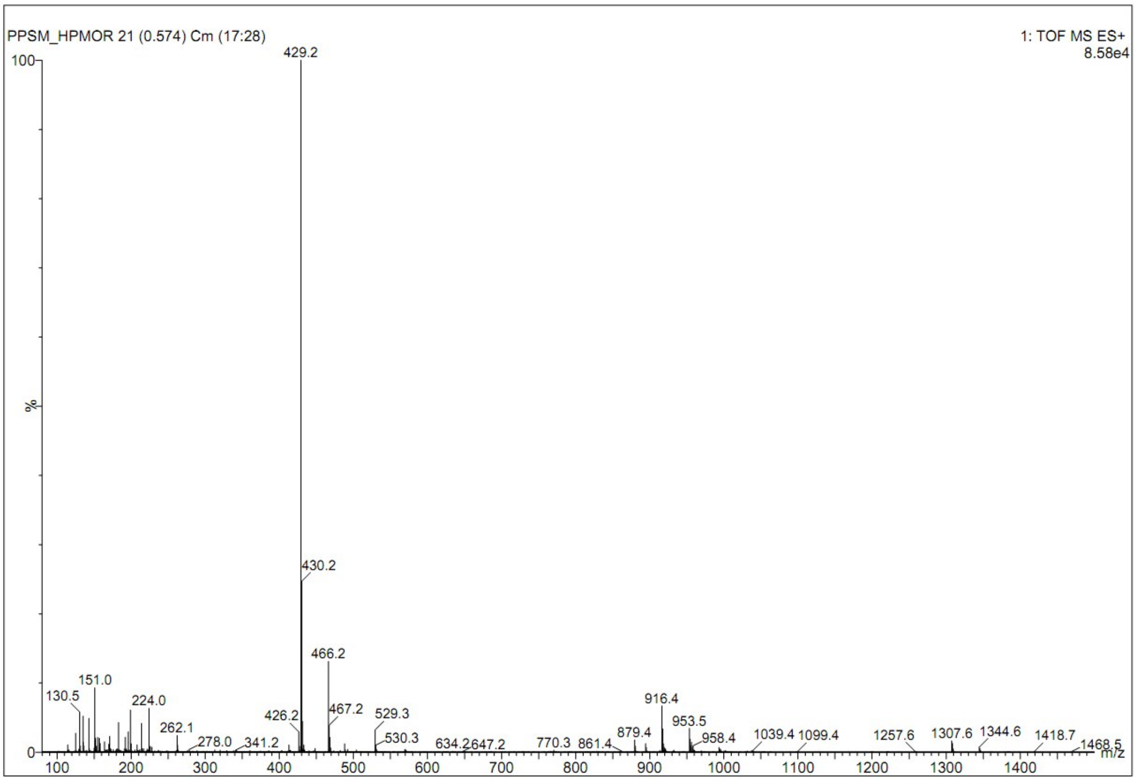


Elemental Composition Report Page 1 of 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
1538 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 1-120 H: 1-150 N: 0-15 O: 0-20
PPSM_HPET 34 (0.857) Cm (34:42)
1: TOF MS ES+

Figure S10: 2,5,8-trimorpholino-heptazine (**2a**)



Elemental Composition Report **Page 1 of 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
822 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 1-120 H: 1-150 N: 0-10 O: 0-20
PPSM_HPMOR 21 (0.574) Cm (17:28)
1: TOF MS ES+

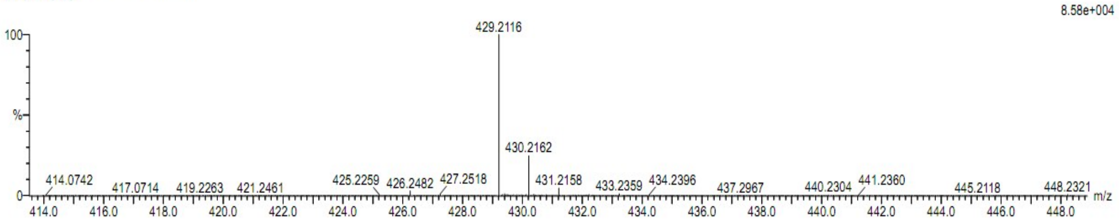
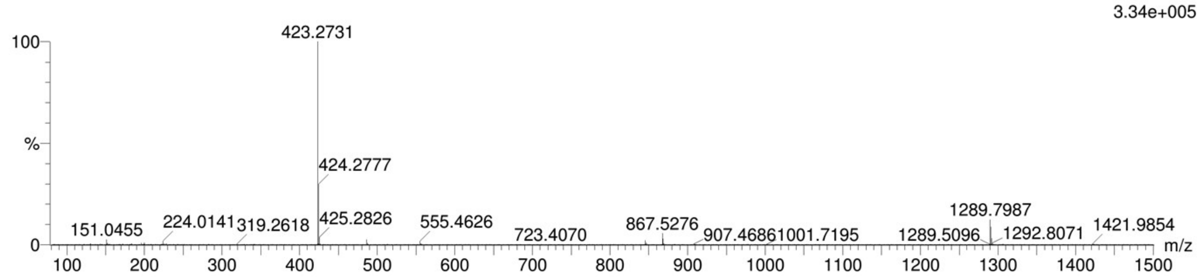


Figure S11: 2,5,8-tri(piperidin-1-yl)-heptazine (**2b**)

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
53 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-36 H: 0-56 N: 0-10

28-Jan-2019 14:02:20 LCT Premier XE KE483 MASSON_le27-3 20 (0.536) Cm (14:32)
1: TOF MS ES+



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Minimum:                                      -1.5
Maximum:                    10.0      5.0     100.0

Mass       Calc. Mass       mDa       PPM     DBE       i-FIT      i-FIT (Norm) Formula

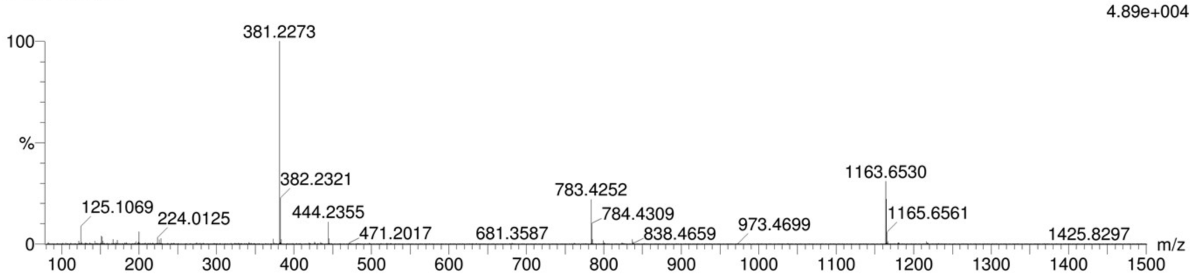
423.2731   423.2733         -0.2      -0.5    11.5      1327.0     0.0          C21  H31  N10
```

Figure S12: 2,5,8-tri(pyrrolidin-1-yl)-heptazine (**2c**)

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
38 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-36 H: 0-40 N: 0-10

28-Jan-2019 13:55:47
1: TOF MS ES+
LCT Premier XE KE483
MASSON_le27-1 21 (0.572) Cm (14:29)



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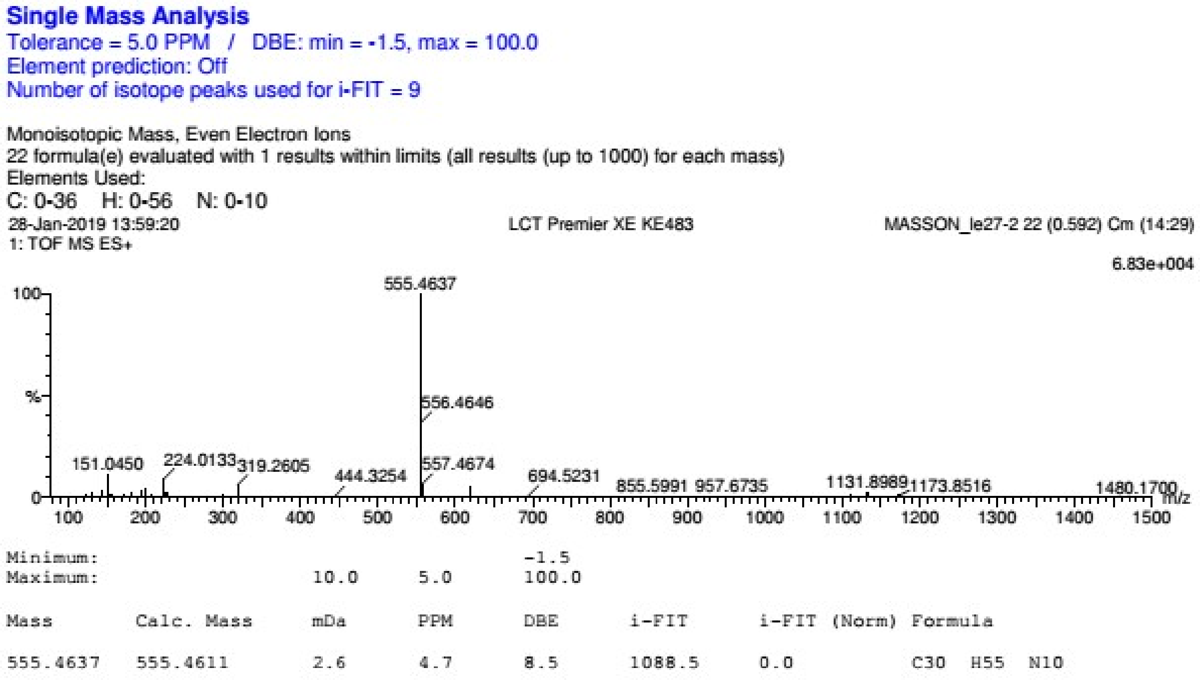
Minimum:                                        -1.5
Maximum:                    10.0      5.0       100.0

Mass        Calc. Mass      mDa       PPM       DBE       i-FIT      i-FIT (Norm) Formula

381.2273    381.2264        0.9       2.4       11.5      1018.0     0.0          C18  H25  N10
```

Figure S13 : 2,5,8-tris(2-ethylhexyl-1-amine)-heptazine (**2d**)



Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
22 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-36 H: 0-56 N: 0-10

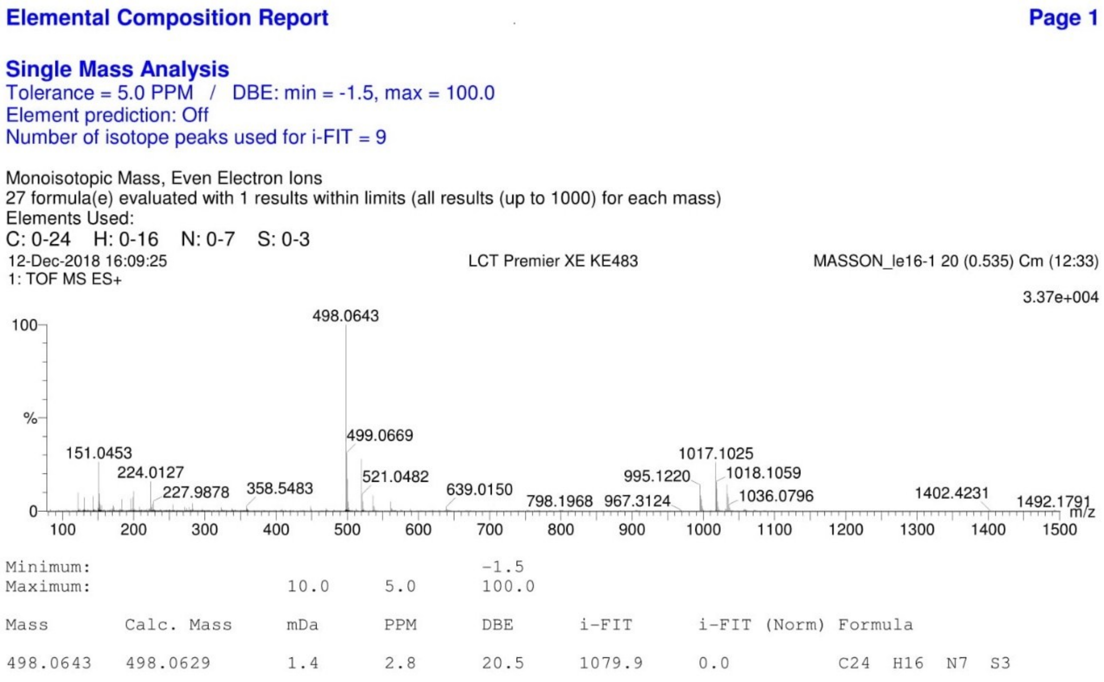
28-Jan-2019 13:59:20 LCT Premier XE KE483 MASSON_le27-2 22 (0.592) Cm (14:29)
1: TOF MS ES+

```
Minimum:                                       -1.5
Maximum:                   10.0      5.0       100.0

Mass       Calc. Mass      mDa       PPM       DBE       i-FIT      i-FIT (Norm) Formula

555.4637   555.4611        2.6       4.7       8.5       1088.5     0.0          C30  H55  N10
```

Figure S14 : 2,5,8-tris(phenylthio)-heptazine (**3b**)



Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
27 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-24 H: 0-16 N: 0-7 S: 0-3

12-Dec-2018 16:09:25 LCT Premier XE KE483 MASSON_le16-1 20 (0.535) Cm (12:33)
1: TOF MS ES+

```
Minimum:                                      -1.5
Maximum:                   10.0      5.0      100.0

Mass       Calc. Mass      mDa       PPM      DBE       i-FIT      i-FIT (Norm) Formula

498.0643   498.0629        1.4       2.8      20.5      1079.9     0.0          C24  H16  N7  S3
```

Figure S15: 2,5,8-tris(benzylthio)-heptazine (**3c**)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 9

Monoisotopic Mass, Even Electron Ions
27 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-27 H: 0-22 N: 0-7 S: 0-3

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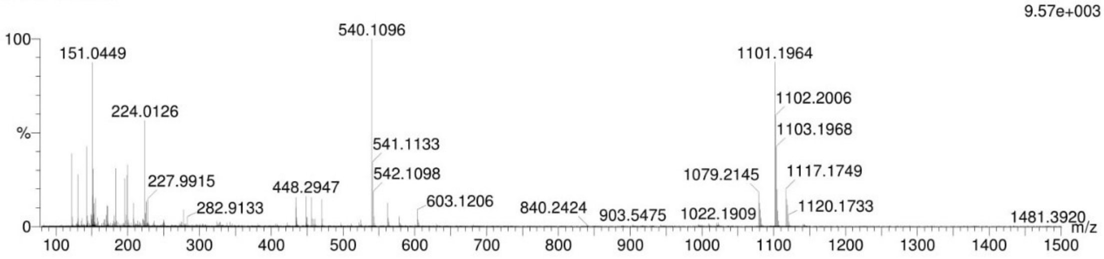
1: TOF MS ES+



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Minimum:                                    -1.5
Maximum:                   10.0      5.0    100.0

Mass       Calc. Mass      mDa       PPM    DBE      i-FIT     i-FIT (Norm) Formula

540.1096   540.1099        -0.3      -0.6   20.5     824.7     0.0          C27  H22  N7  S3
```

2. X-Rays structure

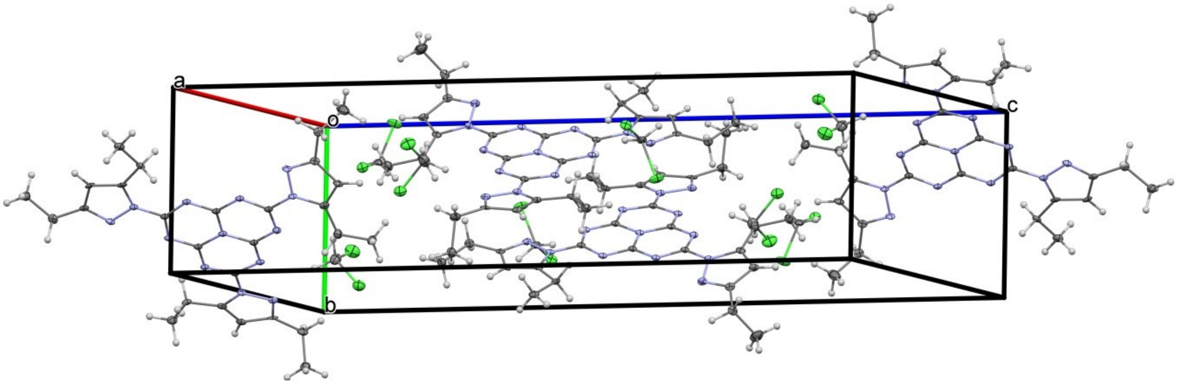

Fig. S16. View of crystal packing of RX in lattice.

Crystals of 2,5,8-tris(3,5-diethyl-pyrazolyl)-heptazine (**1**) suitable for single crystal X-ray diffraction were obtained from a concentrated dissolution in CH_2Cl_2. The white color of the crystals is probably due to solvents loss on the surface.

X-ray diffraction data for compound **1** were collected by using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IuS source Mo **Kα** radiation. Crystal was mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. For compounds, the temperature of the crystal was maintained at the selected value by means of an N-Helix Cryosystem cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[1] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018[2] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[3]

The crystal data collection and refinement parameters are given in Table S1.

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1) Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, **1997**.

2) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., **2008**, 64, 112-122

3) Farrugia, L. J. *J. Appl. Cryst*., **1999**, *32*, 837.

CCDC 1843875 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

Table S1. Crystallographic data and structure refinement details.

Compound	**1**
	CCDC 1843875
Empirical Formula	$C_{27} H_{33} N_{13}$, $2(CH_2Cl_2)$
M_r	709.51
Crystal size, mm^3	0.14 x 0.10 x 0.08
Crystal system	monoclinic
Space group	$P\,2_1/n$
a, Å	14.366(3)
b, Å	7.9689(17)
c, Å	30.185(6)
α, °	90
β, °	100.386(6)
γ, °	90
Cell volume, Å^3	3399.0(12)
Z ; Z'	4 ; 1
T, K	100(1)
Radiation type ; wavelength Å	MoKα ; 0.71073
F_{000}	1480
μ, mm^{-1}	0.391
θ range, °	2.290 - 23.918
Reflection collected	57 618
Reflections unique	5 147
R_{int}	0.2313
GOF	1.084
Refl. obs. ($I>2\sigma(I)$)	2 928
Parameters	349
wR_2 (all data)	0.2120
R value ($I>2\sigma(I)$)	0.0906
Largest diff. peak and hole (e-.Å^{-3})	0.454 ; -0.485

3. Photophysical studies

Generalities

Absorption spectra were recorded on a double beam CARY 100 spectrometer in 1cm cuvettes. Fluorescence emission spectra were obtained on a Fluoromax-3 from Horiba Jobin-Yvon, with xenon light source. The signal was collected at 90° with respect to the excitation beam. Fluorescence quantum yields were determined using a solution of quinine sulfate dissolved in H_2SO_4 0.5M as reference. Fluorescence emission spectra were recorded using excitation wavelength varying between 300 and 320 nm, at concentrations ensuring that the OD is below 0.1 at the excitation wavelength and below, to avoid reabsorption artifacts. This corresponds to concentrations between 1 and 3 µM for heptazines **1** and **3a-3c** and to concentrations between 36 and 46 µM for heptazines **2a-2d**. Molar extinction coefficients measurements confirm a good solubility of all heptazines in dichloromethane up to 50µM (we suppose the solubility remains good at much higher concentrations but this corresponds to OD>3 where the detector of the UV spectrometer saturates).

UV-Vis absorption spectra at 50µM in DCM

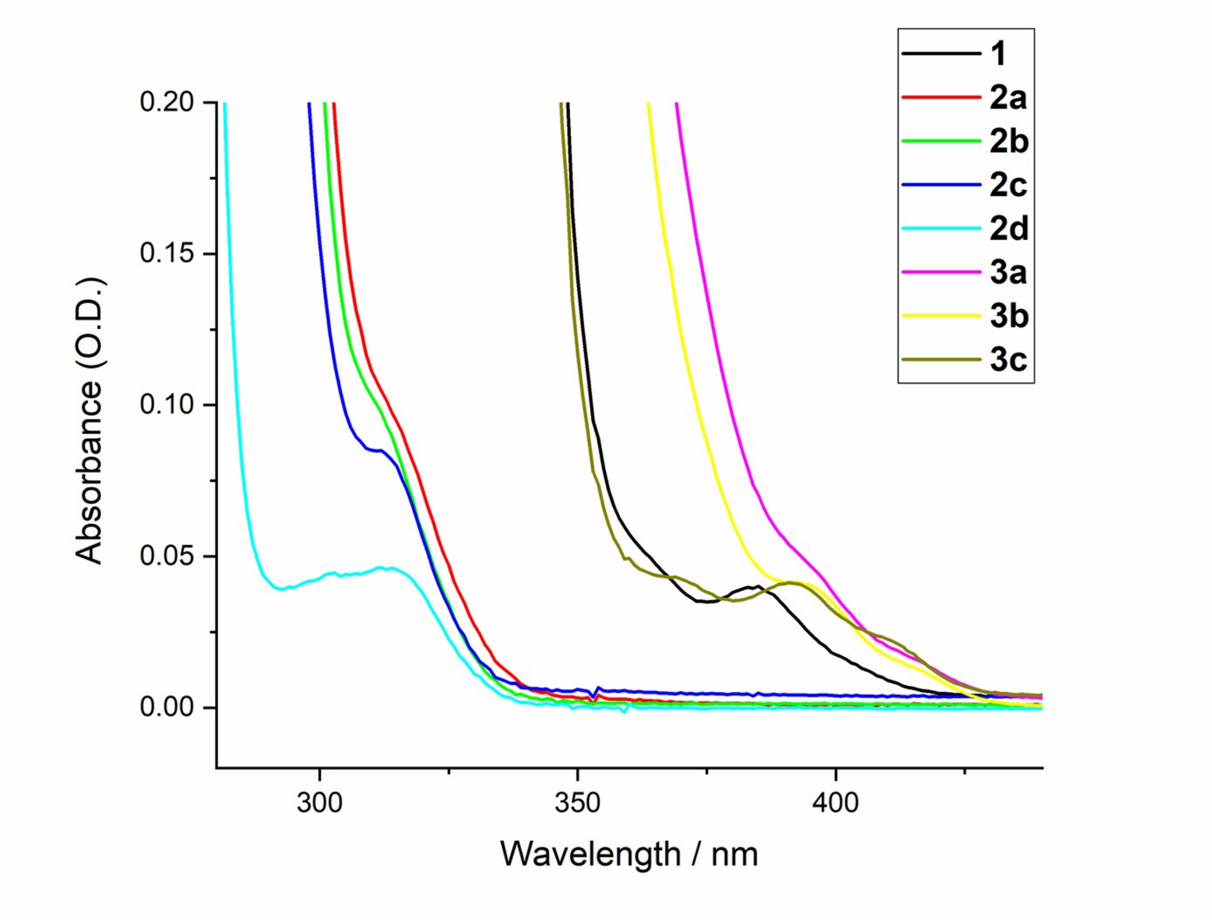


Figure S17: Low energy transitions for heptazines **1-3**. Spectra are recorded at 50µM in dichloromethane.

Solvatochromism

Table S2: influence of the solvent on the absorption and emission maxima of selected heptazines.

solvent	**1**		**2a**		**3b**		**3c**	
	λmax abs (nm)	λmax emiss (nm)	λmax abs (nm)	λmax emiss (nm)	λmax abs (nm)	λmax emiss (nm)	λmax abs (nm)	λmax emiss (nm)
DCM	314	459	272	386	301	578	319	450
CH_3CN	300	454	271	383	300	455/613	310	nd
EtOH	291	357	272	385	300	452	291	356
$CHCl_3$	315	454	273	382	302	565	321	449
Dioxane	302	463	273	388	301	513	315	451
THF	302	463	273	391	302	556	312	452

Solid-state fluorescence

Solid state fluorescence emission spectra have been recorded on thin films obtained by dropcasting a DCM solution on a microscope glass slide cleaned by thorough rinsing with ethanol.

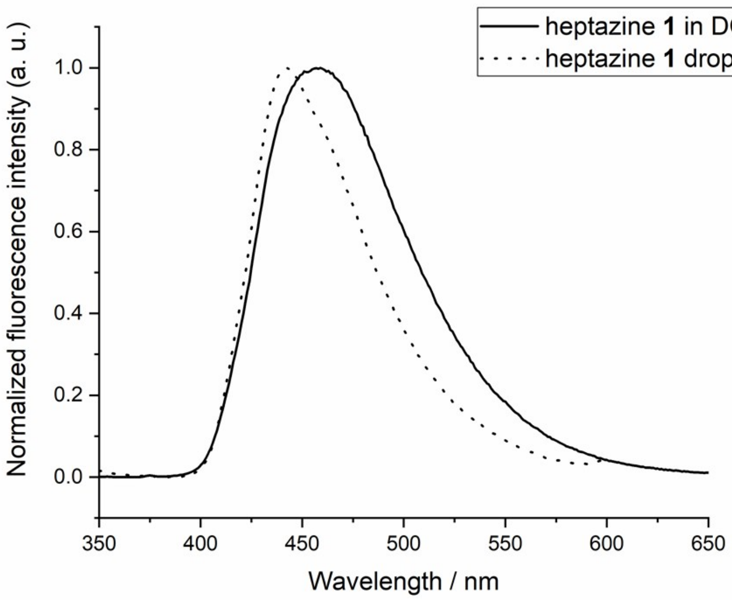


Figure S18: fluorescence emission of heptazine **1** in DCM solution (solid line) and dropcasted on a glass coverslide (dotted line). The shift of the emission maximum is -16nm between the solution and the solid state

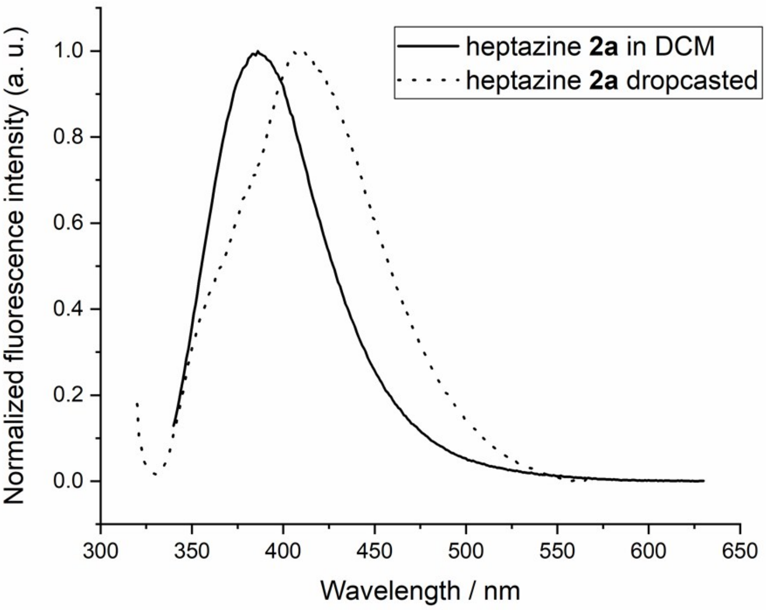


Figure S19: fluorescence emission of heptazine **2a** in DCM solution (solid line) and dropcasted on a glass coverslide (dotted line). The shift of the emission maximum is +25nm between the solution and the solid state.

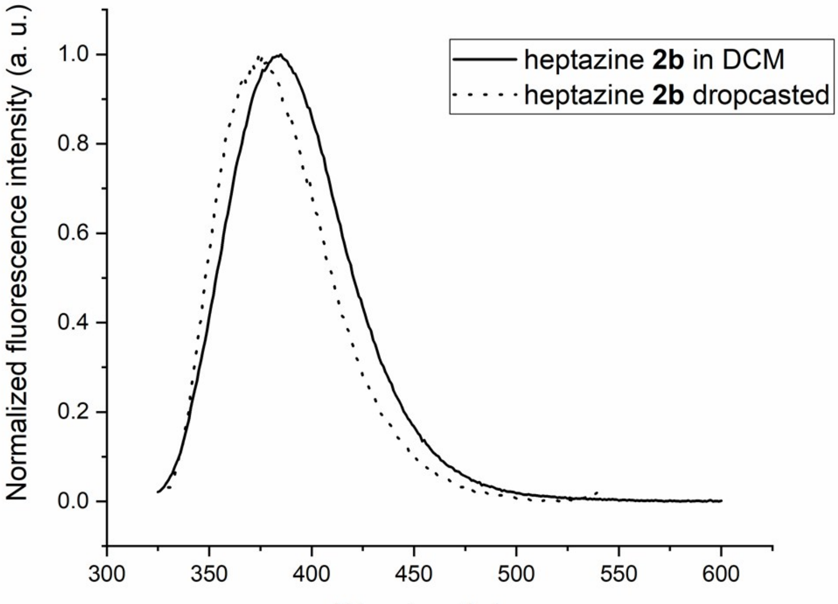


Figure S20: fluorescence emission of heptazine **2b** in DCM solution (solid line) and dropcasted on a glass coverslide (dotted line). The shift of the emission maximum is -9 nm between the solution and the solid state.

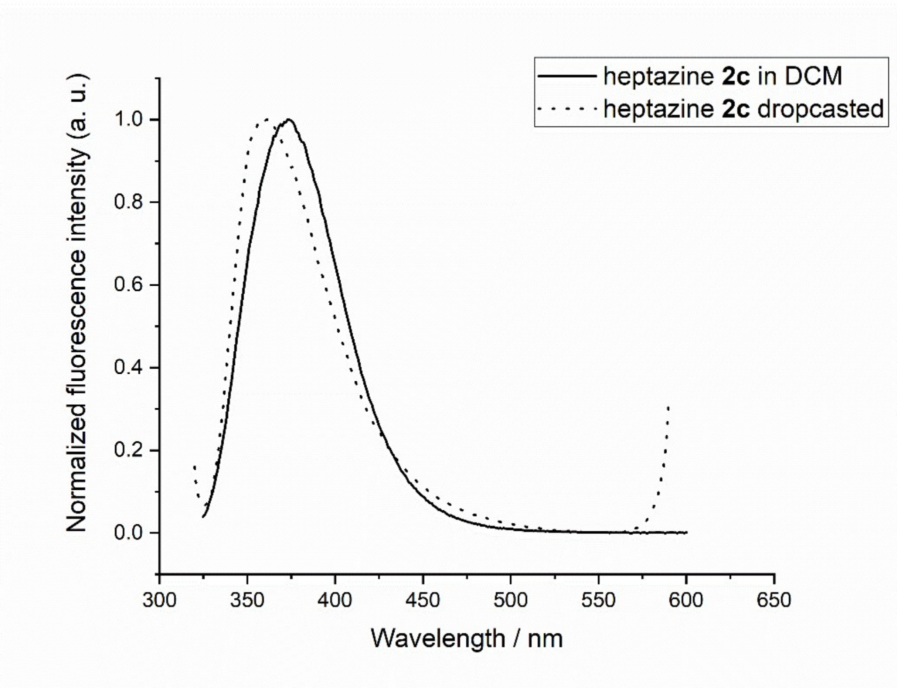


Figure S21: fluorescence emission of heptazine **2c** in DCM solution (solid line) and dropcasted on a glass coverslide (dotted line). The shift of the emission maximum is -13 nm between the solution and the solid state.

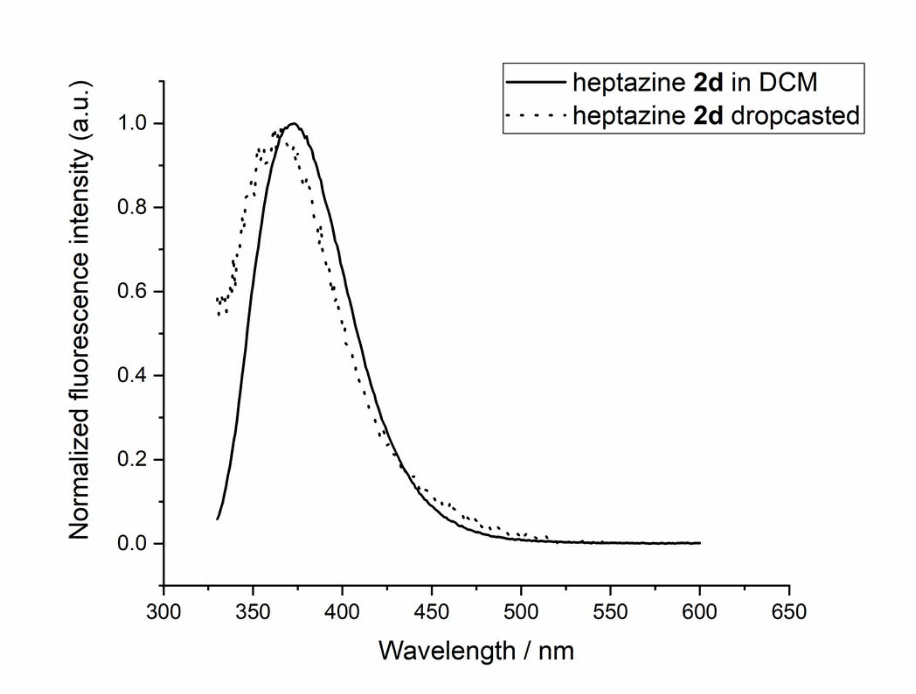


Figure S22: fluorescence emission of heptazine **2d** in DCM solution (solid line) and dropcasted on a glass coverslide (dotted line). The shift of the emission maximum is -7 nm between the solution and the solid state.

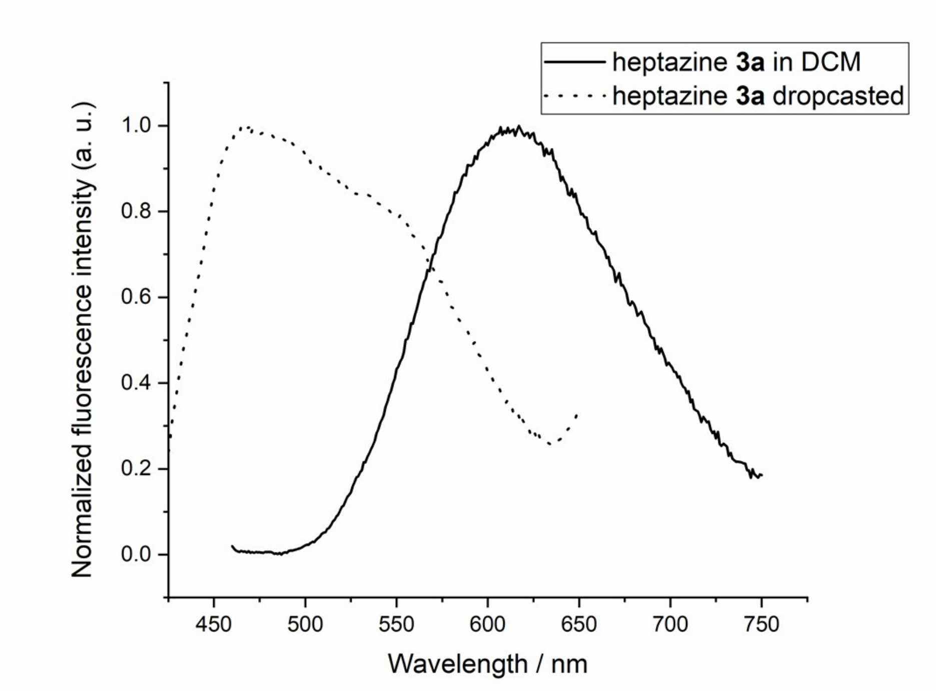


Figure S23: fluorescence emission of heptazine **3a** in DCM solution (solid line) and dropcasted on a glass coverslide (dotted line). The shift of the emission maximum is -152 nm between the solution and the solid state.

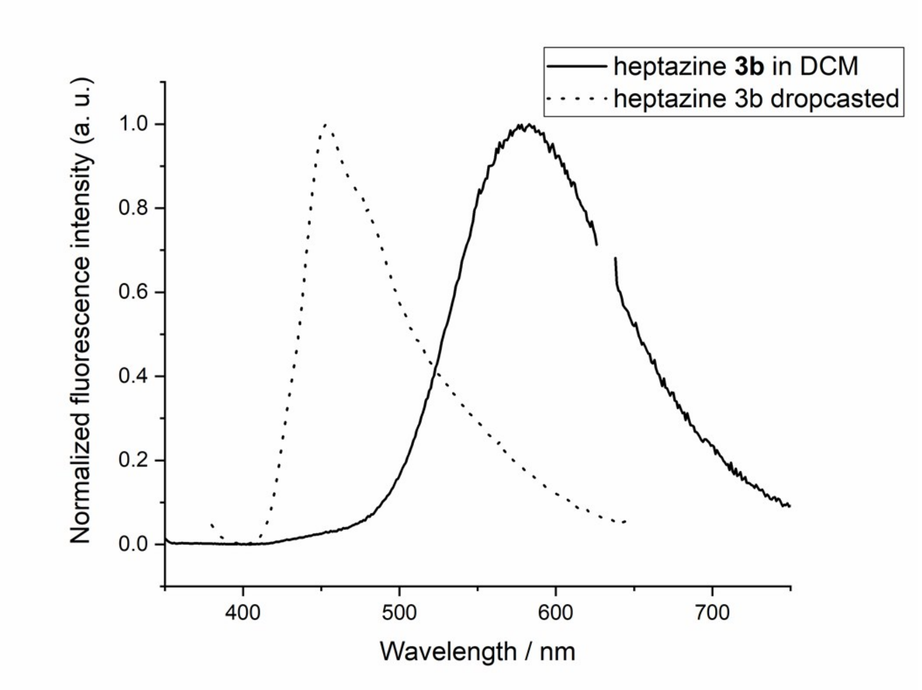


Figure S24: fluorescence emission of heptazine **3b** in DCM solution (solid line) and dropcasted on a glass coverslide (dotted line). The shift of the emission maximum is -129nm between the solution and the solid state.

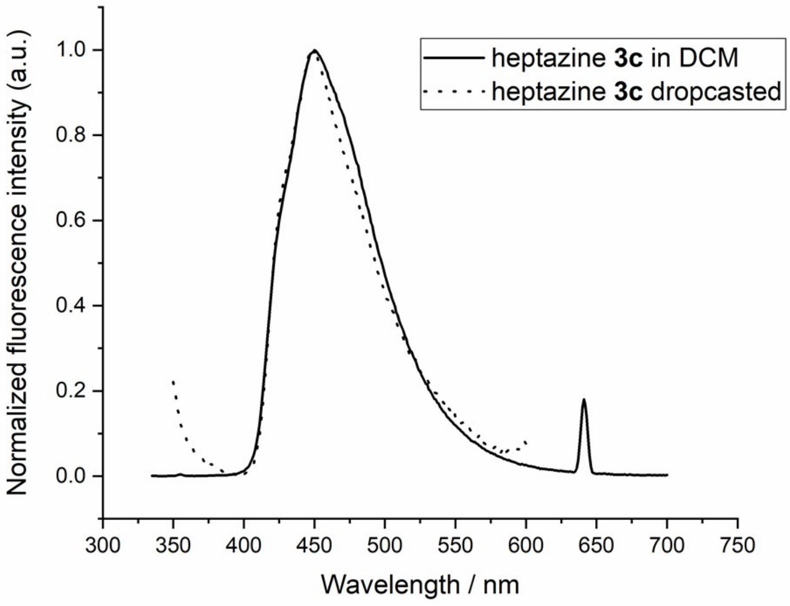


Figure S25: fluorescence emission of heptazine **3c** in DCM solution (solid line) and dropcasted on a glass coverslide (dotted line). The shift of the emission maximum is 0 nm between the solution and the solid state.

4. Electrochemical studies

Electrochemical studies were performed using DCM as a solvent, with *N*-tetrabutylammonium hexafluorophosphate (Fluka, puriss.) as the supporting electrolyte. The substrate concentration was ca. 2 mM. A 2 mm glassy carbon electrode was used as the working electrode, along with a Ag/AgCl pseudo-reference electrode and a Pt wire counter electrode. The cell was connected to a PAR 273A potentiostat. The reference electrode was checked *vs*. ferrocene as recommended by IUPAC. All solutions were degassed by argon bubbling prior to each experiment.

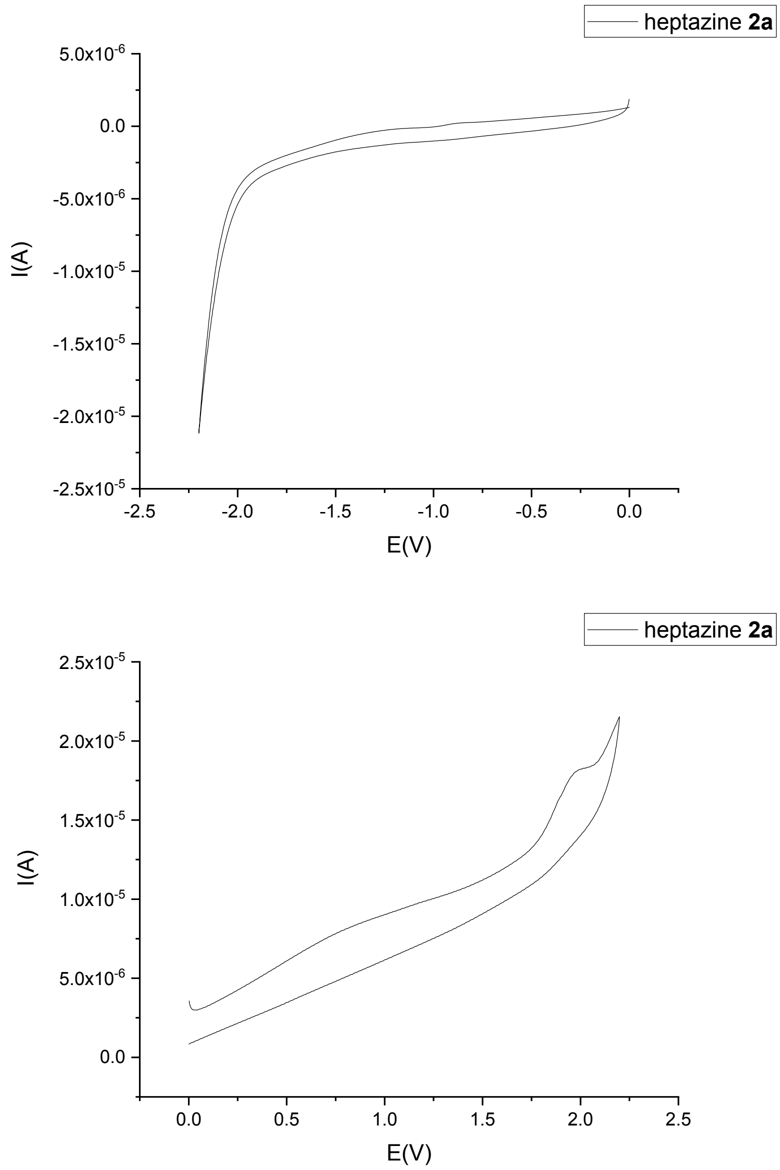
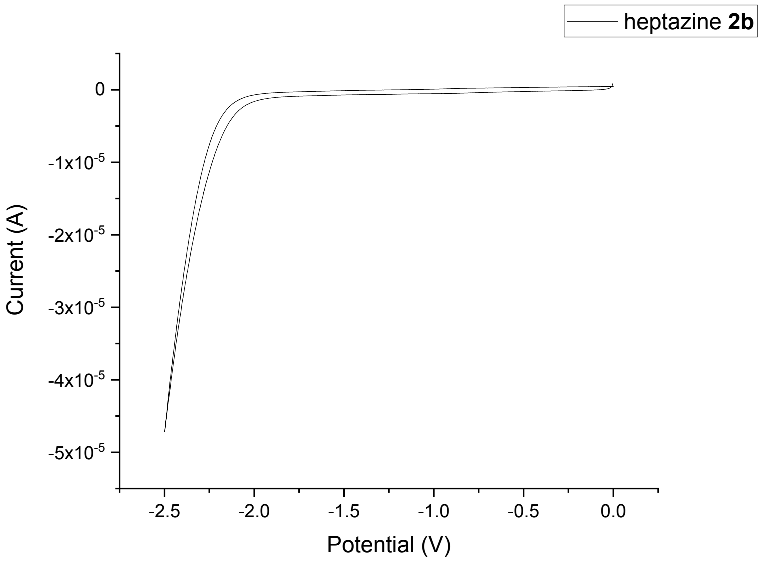


Figure S26: cyclovoltamogramms of heptazine **2a** (E°(Fc+/Fc)=0.38V)



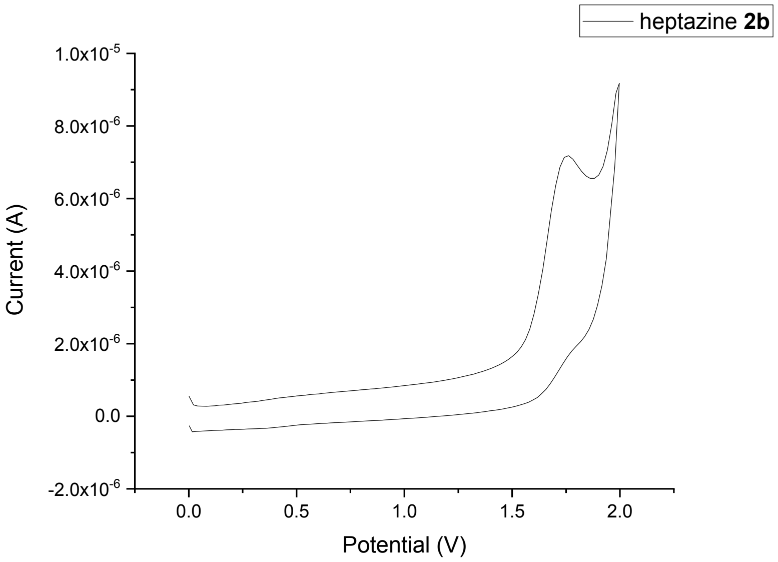


Figure S27: cyclovoltamogramms of heptazine **2b** (E°(Fc+/Fc)=0.40V)

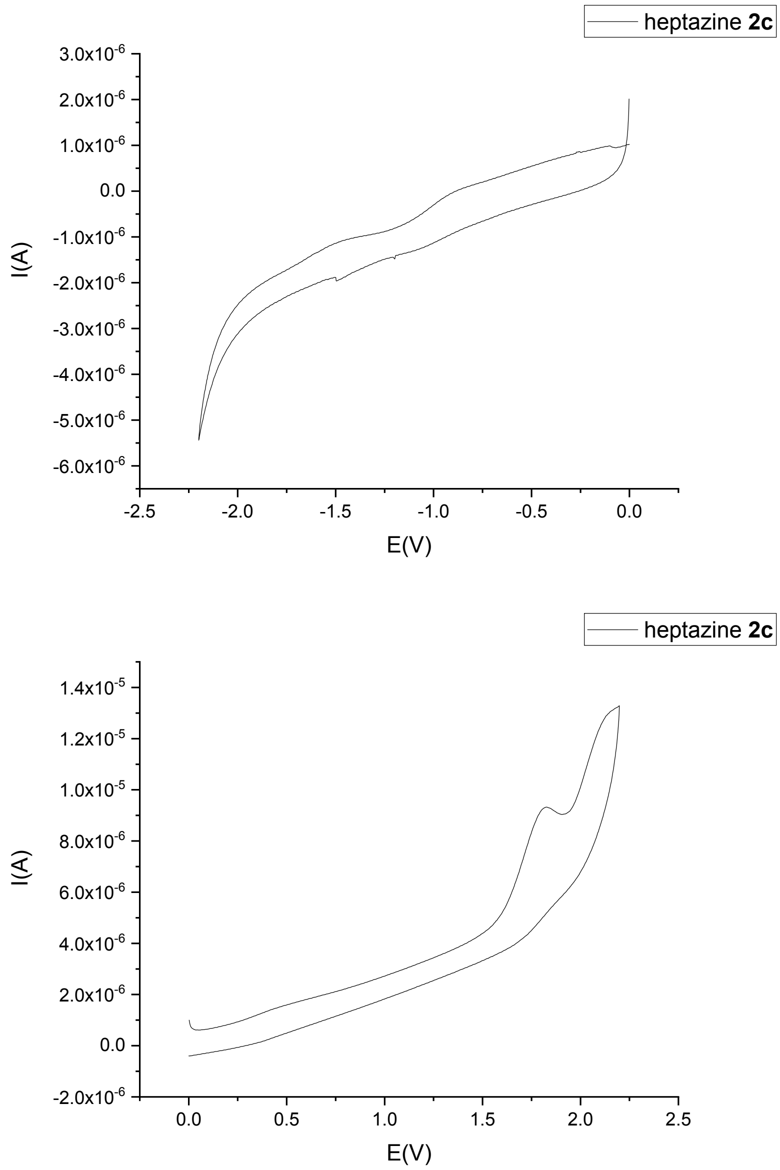
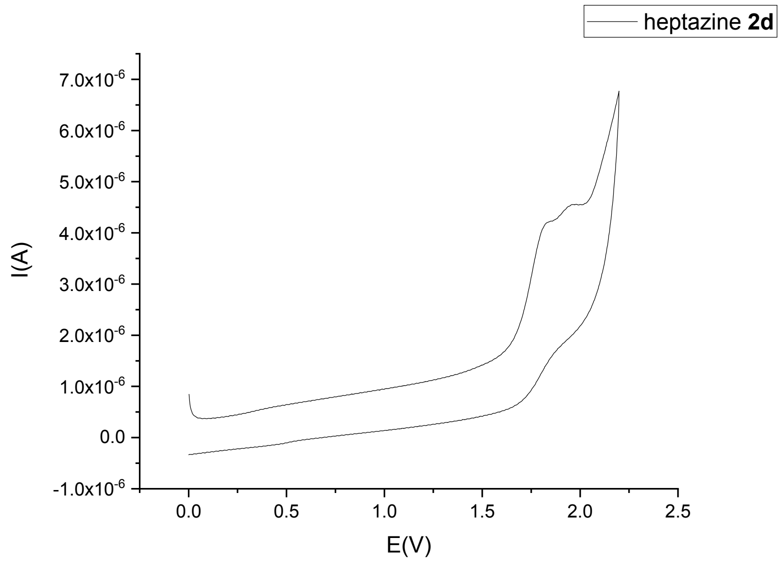


Figure S28: cyclovoltamogramms of heptazine **2c** (E°(Fc+/Fc)=0.38V).



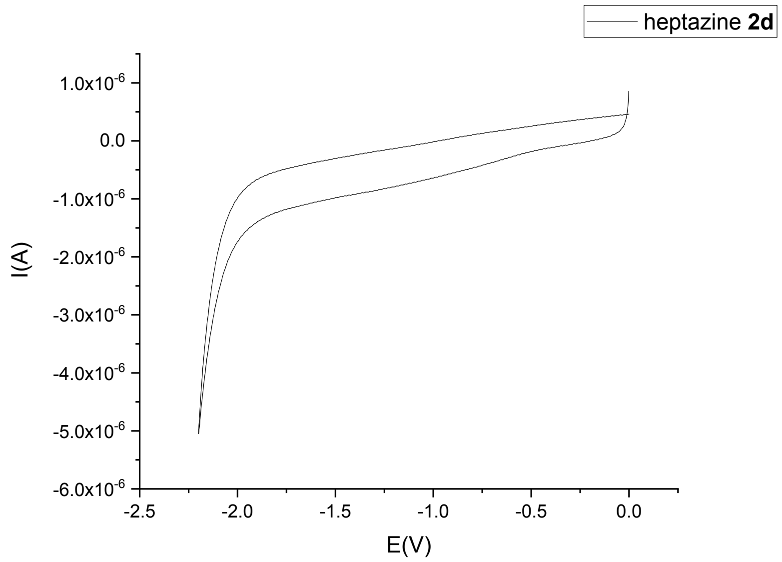


Figure S29: cyclovoltamogramms of heptazine **2d** (E°(Fc+/Fc)=0.38V).

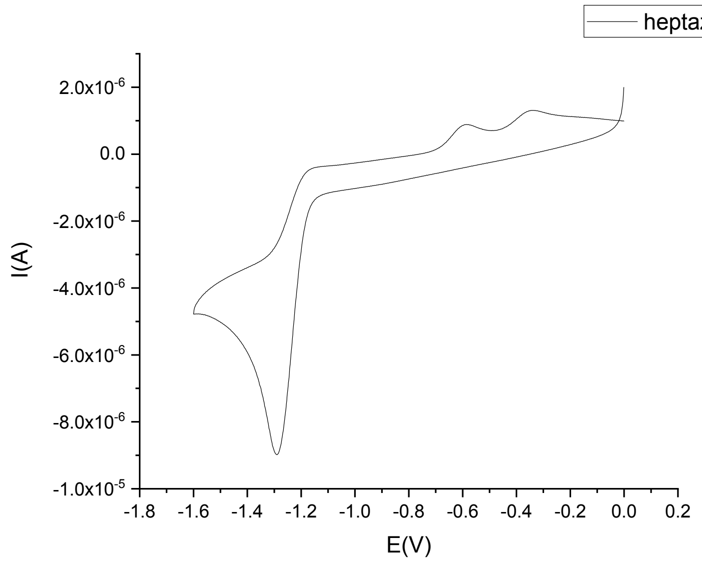


Figure S30: cyclovoltamogramm of heptazine **3b** (E°(Fc+/Fc)=0.40V)

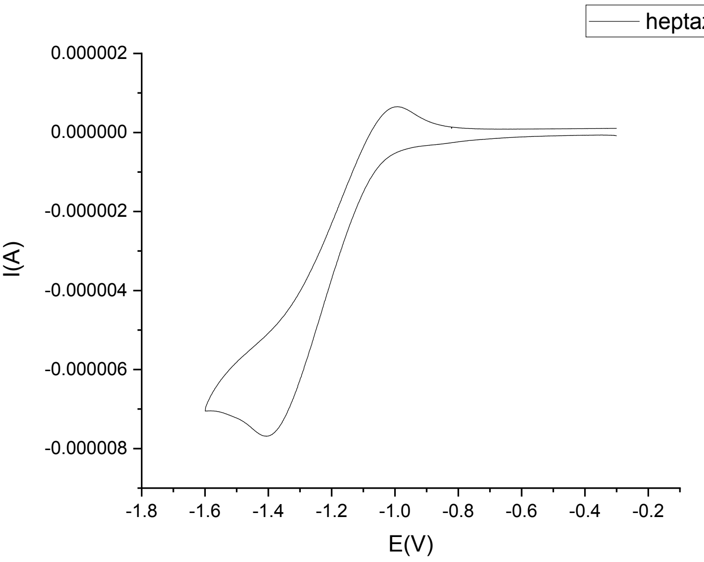
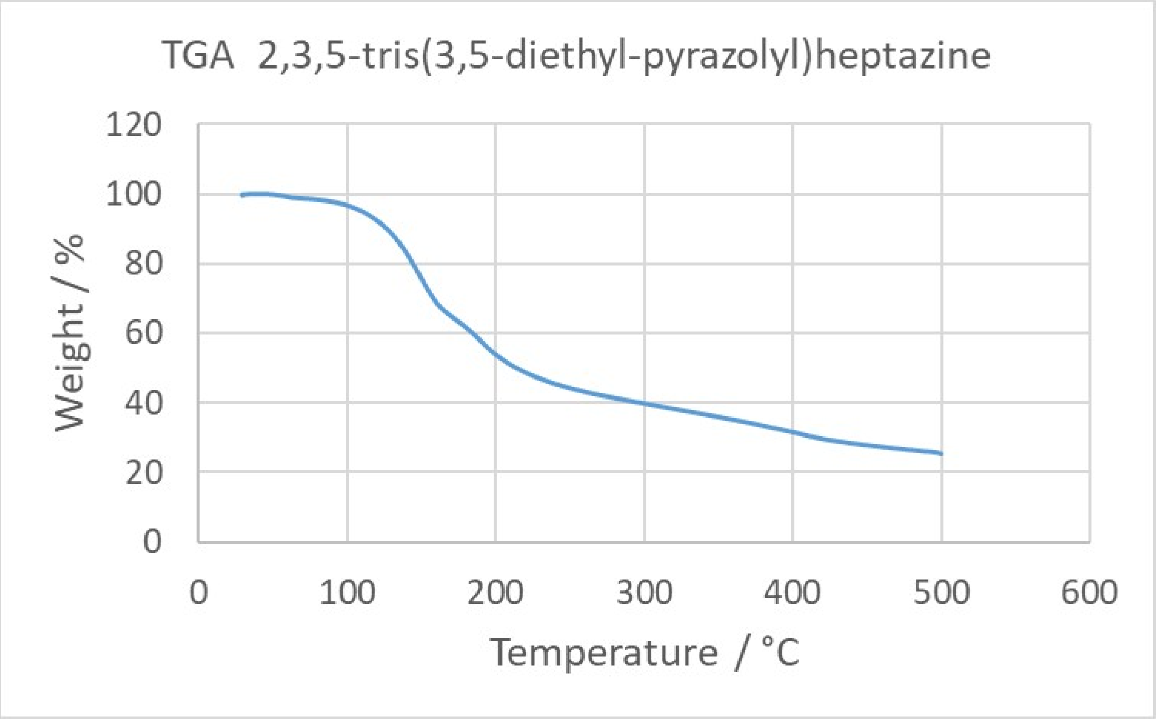


Figure S31: cyclovoltamogramms of heptazine **3c** (E°(Fc+/Fc)=0.65V).

5. ATG analysis of heptazine **1**

Figure S32: The thermal stability was measured by using Thermogravimetric Analysis (TGA, Perkin Elmer, Pyris 6 TGA) in alumina crucible under a nitrogen flow of 150 mL min^{-1} with a heating scan rate of 10°C min^{-1} over the temperature range [30°C – 500°C].



6. DFT calculations

Calculations were performed using the hybrid B3LYP functional, as implemented in Gaussian 09 software package.[2] A 6-31G(d) basis set was used. For geometry optimizations, all minima were verified via a calculation of vibrational frequencies, ensuring that no imaginary frequencies were present.

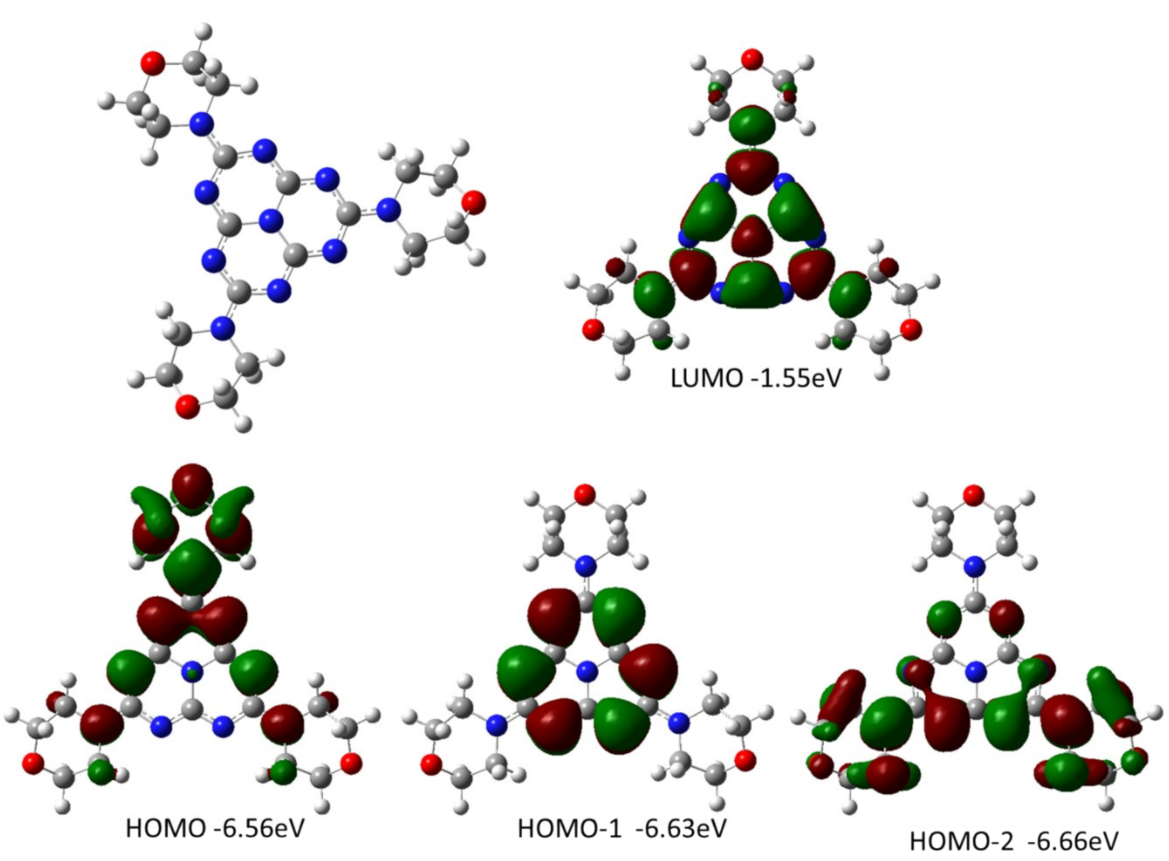
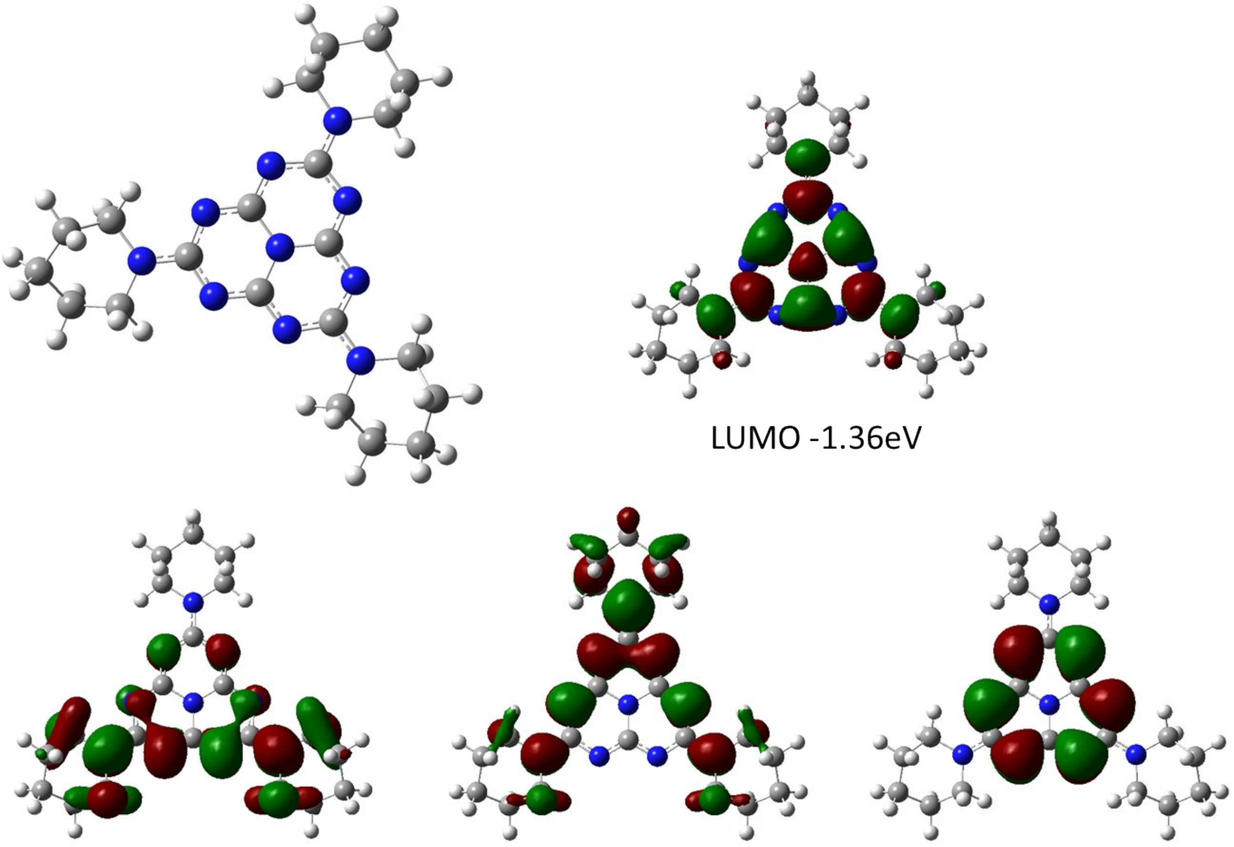


Figure S33: Optimized geometry (B3LYP 6-31G-(d)) together with the representation and energy levels of HOMO-2, HOMO-1, HOMO and LUMO orbitals of 2,5,8-tris(morpholino)-heptazine **2a** (B3LYP 6.311G+(d,p)).



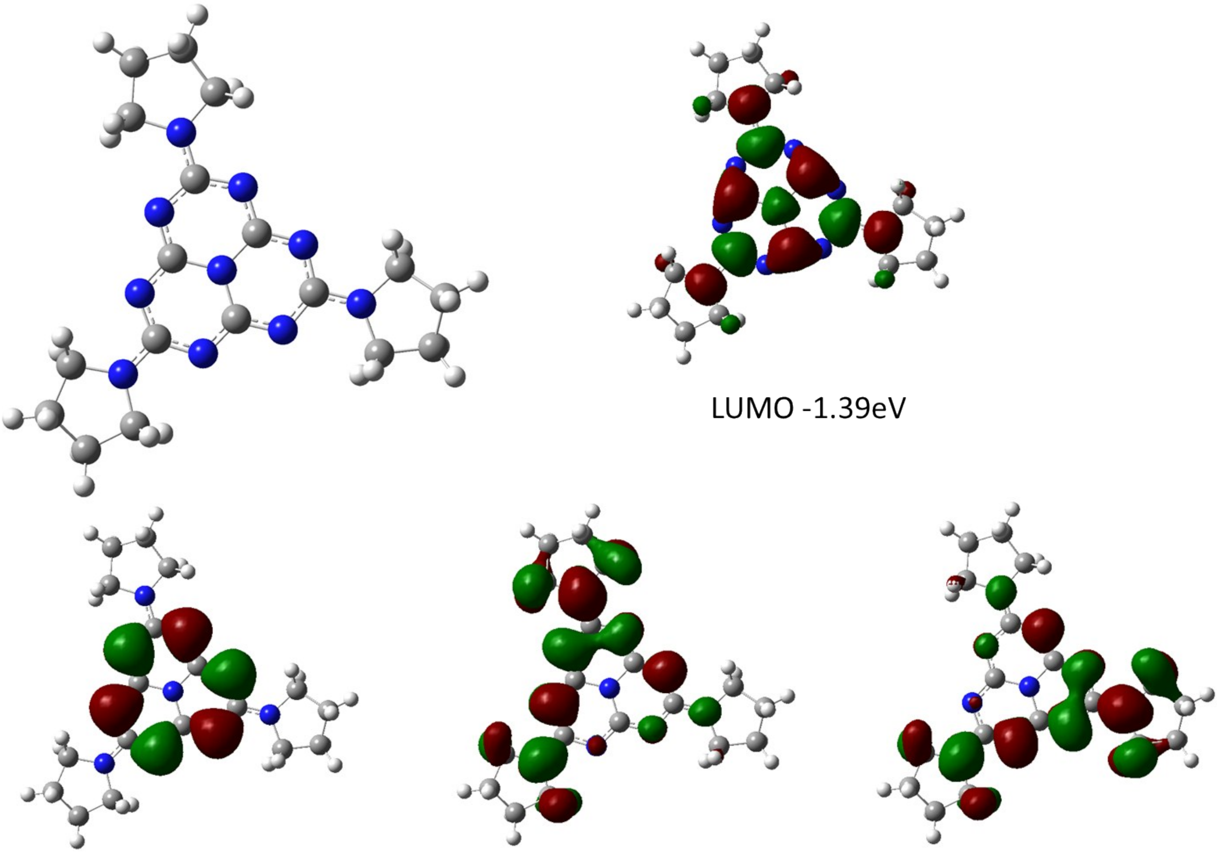
LUMO -1.36eV

HOMO -6.41eV

HOMO-1 -6.42eV

HOMO-2 -6.46eV

Figure S34: Optimized geometry (B3LYP 6-31G-(d)) together with the representation and energy levels of HOMO-2, HOMO-1, HOMO and LUMO orbitals of 2,5,8-tris(piperidino)-heptazine **2b** (B3LYP 6.311G+(d,p)).



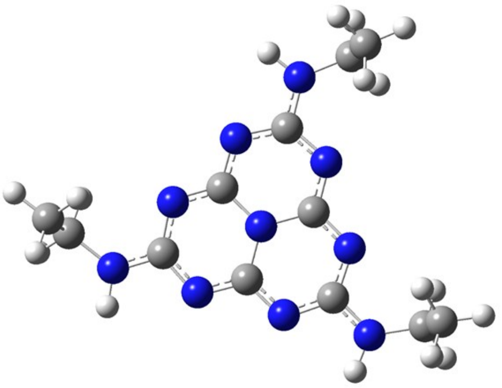
LUMO -1.39eV

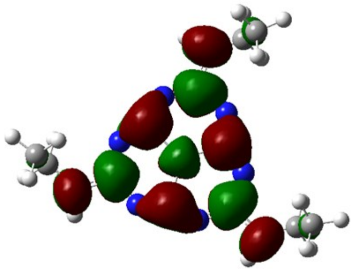
HOMO -6.46eV

HOMO-1 -6.470eV

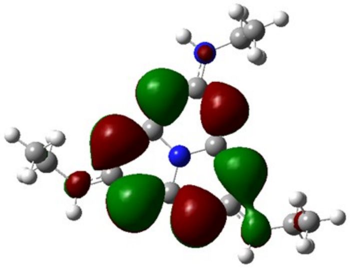
HOMO-2 -6.471eV

Figure S35: Optimized geometry (B3LYP 6-31G-(d)) together with the representation and energy levels of HOMO-2, HOMO-1, HOMO and LUMO orbitals of 2,5,8-tris(piperidino)-heptazine **2c** (B3LYP 6.311G+(d,p)).

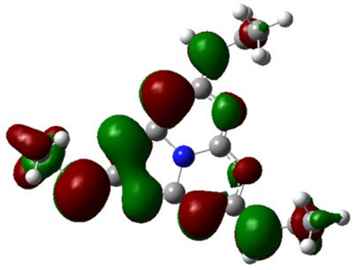




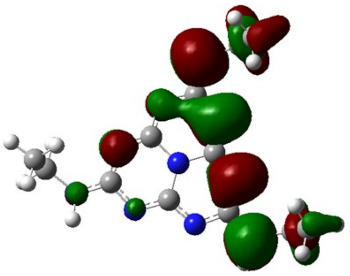
LUMO -1.55eV



HOMO -6.62eV

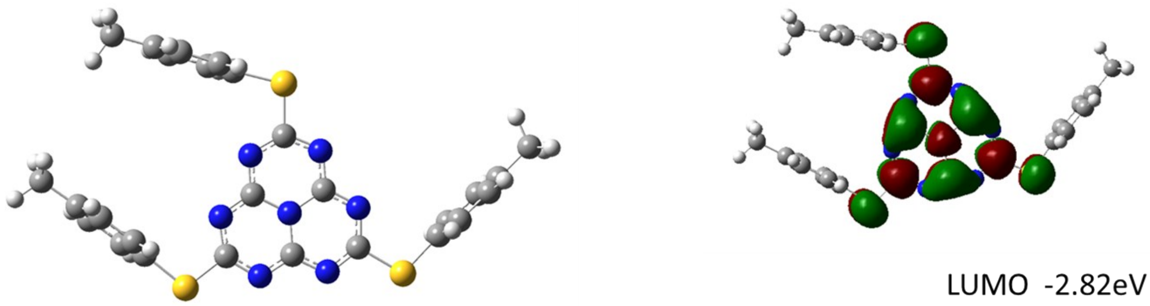


HOMO-1 -6.87eV

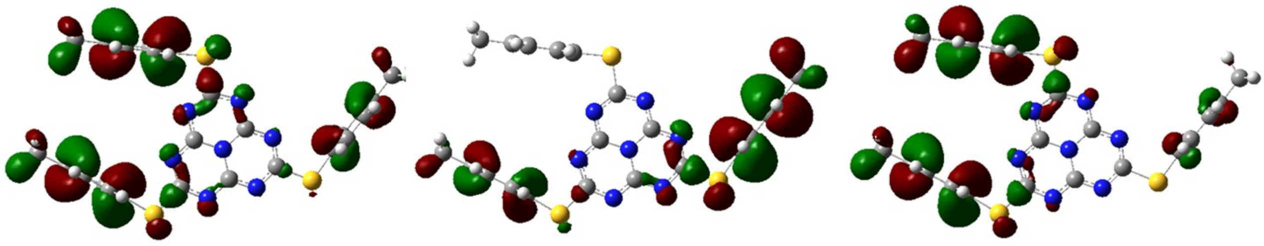


HOMO-2 -6.95eV

Figure S36: Optimized geometry (B3LYP 6-31G-(d)) together with the representation and energy levels of HOMO-2, HOMO-1, HOMO and LUMO orbitals of 2,5,8-tris(ethylamino)-heptazine **2’** (B3LYP 6.311G+(d,p)).

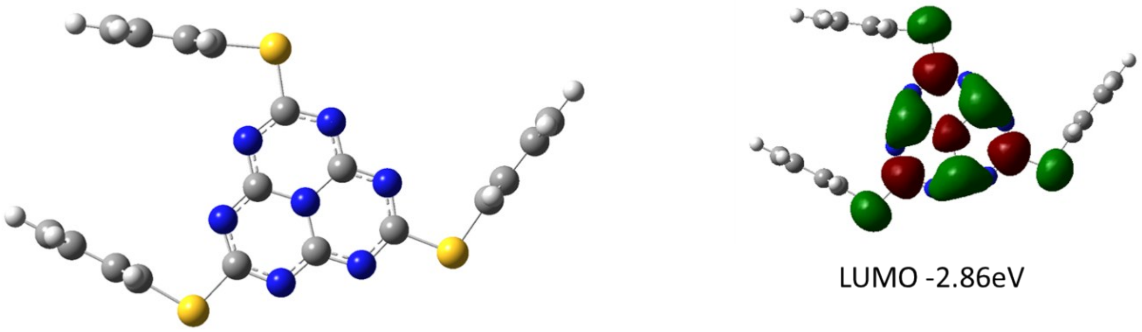


LUMO -2.82eV

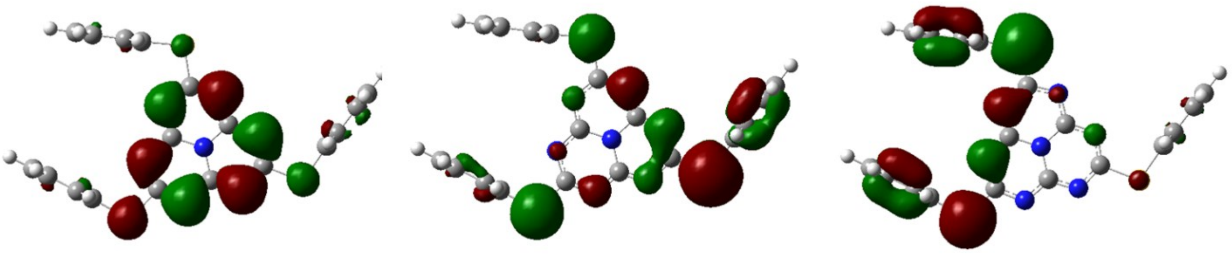


HOMO -7.076eV HOMO-1 -7.080eV HOMO-2 -7.11eV

Figure S37: Optimized geometry (B3LYP 6-31G-(d)) together with the representation and energy levels of HOMO-2, HOMO-1, HOMO and LUMO orbitals of 2,5,8-tris(p-tolylthio)-heptazine **3’** (B3LYP 6.311G+(d,p)).

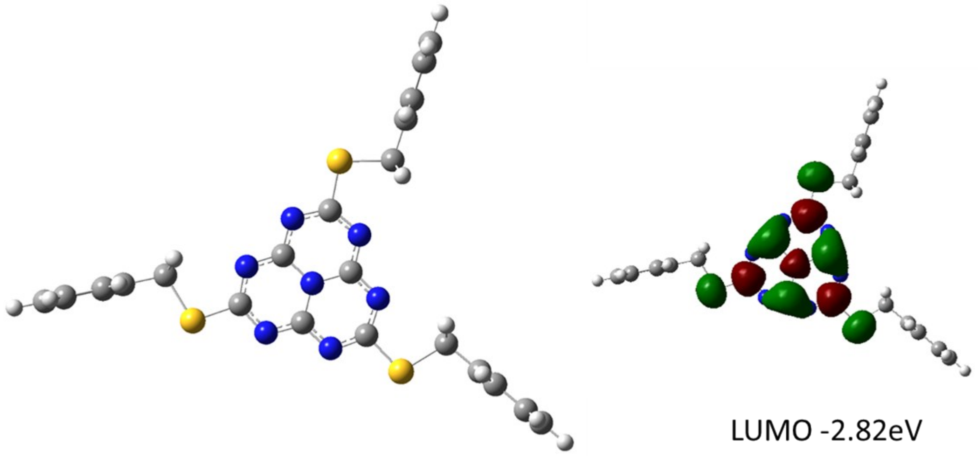


LUMO -2.86eV

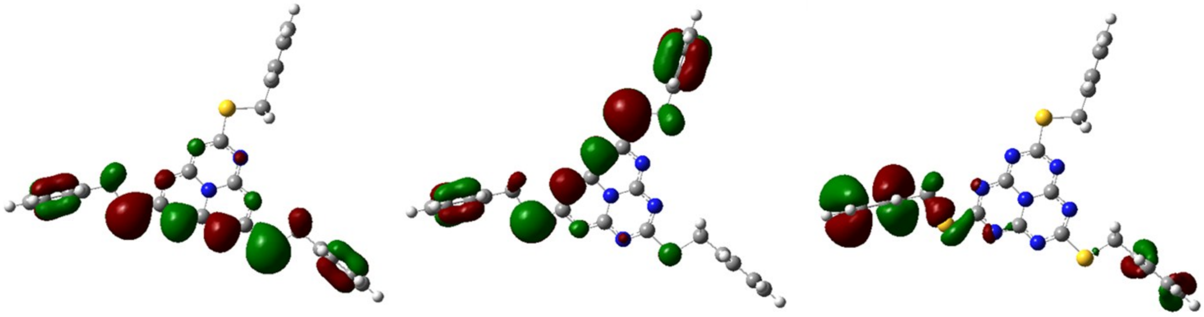


HOMO -7.17 eV HOMO-1 -7.30 eV HOMO-2 -7.32 eV

Fig. S38: Optimized geometry (B3LYP 6-31G-(d)) together with the representation and energy levels of HOMO-2, HOMO-1, HOMO and LUMO orbitals of 2,5,8-tris(phenylthio)-heptazine **3b** (B3LYP 6.311G+(d,p)).



LUMO -2.82eV



HOMO -7.03 eV HOMO-1 -7.10 eV HOMO-2 -7.13 eV

Fig. S39: Optimized geometry (B3LYP 6-31G-(d)) together with the representation and energy levels of HOMO-2, HOMO-1, HOMO and LUMO orbitals of 2,5,8-tris(benzylthio)-heptazine **3c** (B3LYP 6.311G+(d,p)).

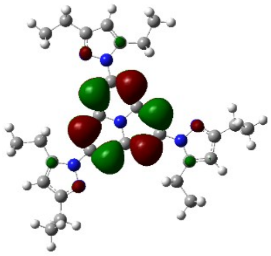
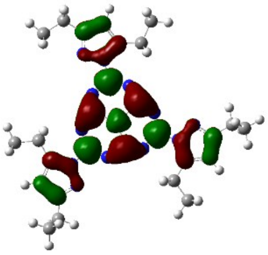
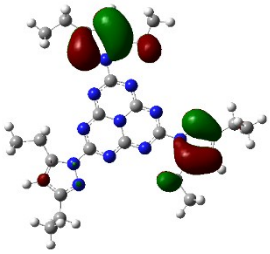
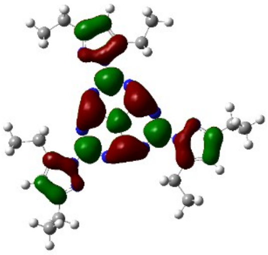
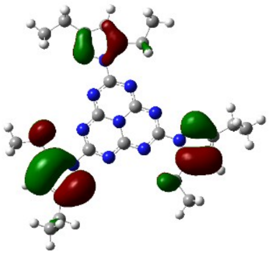
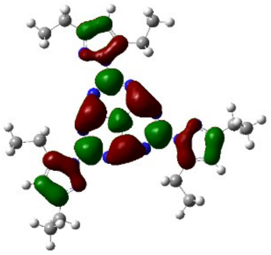
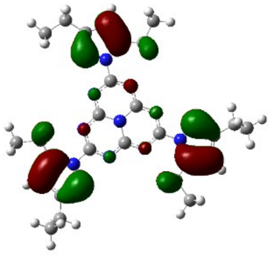
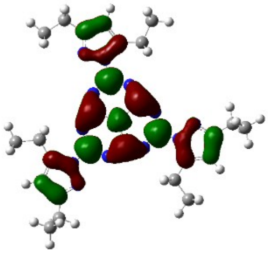
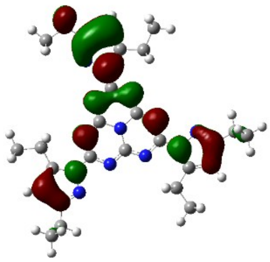
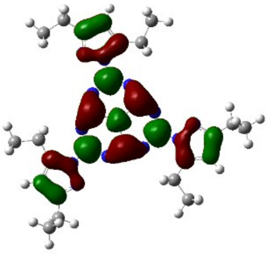
Compound	Excited state	NTO hole	NTO electron
1	1 375 nm f=0		
1	2 333.0 nm f=0.0028		
1	3 332.8 nm f=0.0044		
1	4 331 nm f=0.0007		
1	5 317 nm f=0.8017		

Table S3: vertical absorption transitions computed by TD-DFT and corresponding Natural Transition Orbitals for heptazine **1**.

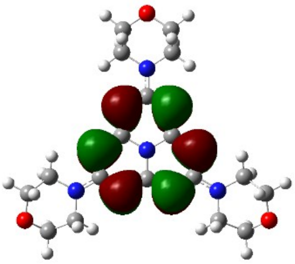
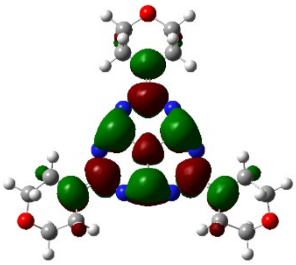
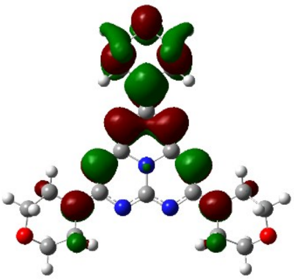
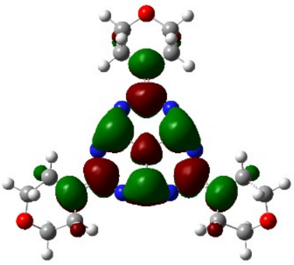
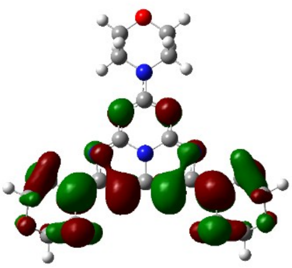
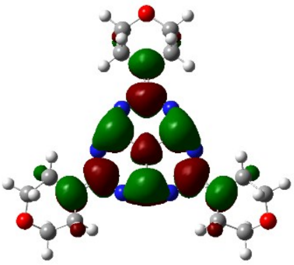
Compound	Excited state	NTO hole	NTO electron
2a	1 308 nm f=0		
2a	2[a] 276 nm f=0.5215	 HOMO	
2a	3[a] 271 nm f=0.4706	 HOMO-2	

Table S4: vertical absorption transitions computed by TD-DFT and corresponding Natural Transition Orbitals for heptazine **2a**.

[a] these transitions imply only one orbital for the hole and one for the electron so NTO analysis was not necessary

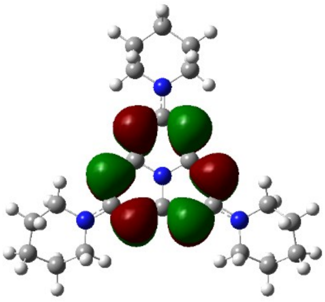
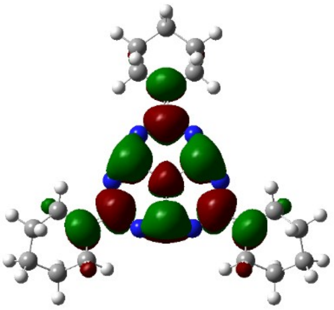
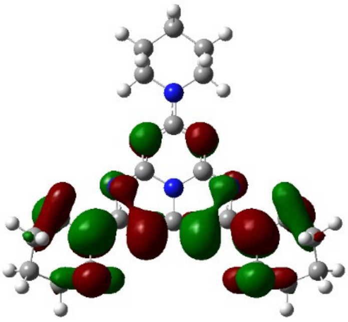
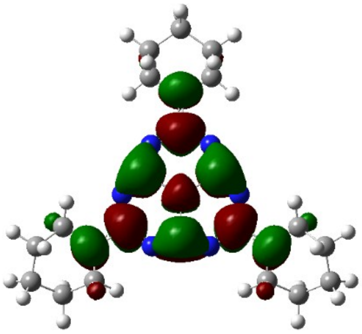
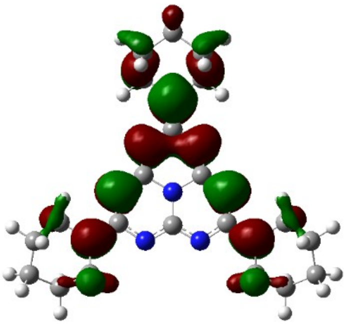
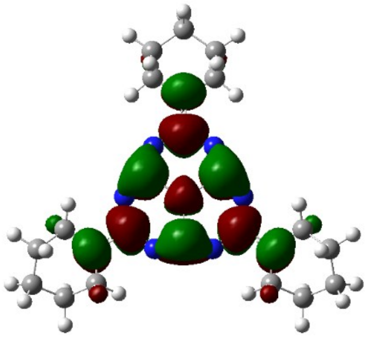
Compound	Excited state	NTO hole	NTO electron
2b	1 308 nm f=0		
2b	2[a] 274.2 nm f=0.482	 HOMO	 LUMO
2b	3[a] 273.5 nm f=0.546	 HOMO-1	

Table S5: vertical absorption transitions computed by TD-DFT and corresponding Natural Transition Orbitals for heptazine **2b**.

[a] these transitions imply only one orbital for the hole and one for the electron so NTO analysis was not necessary

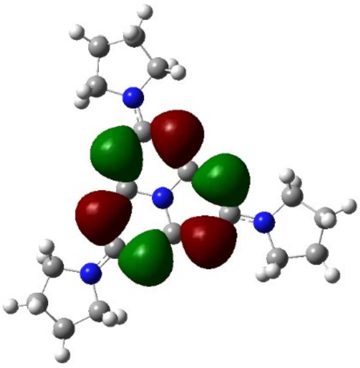
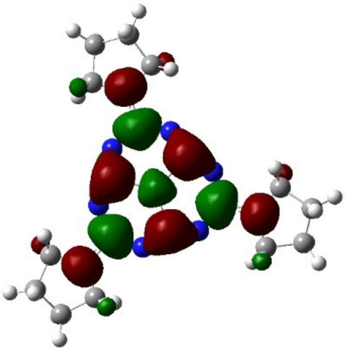
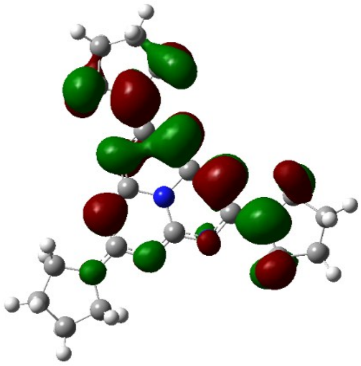
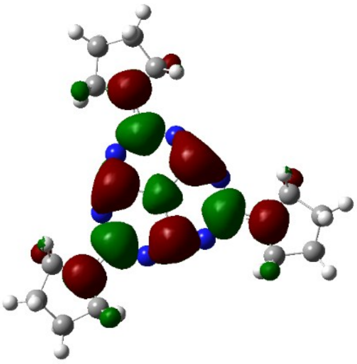
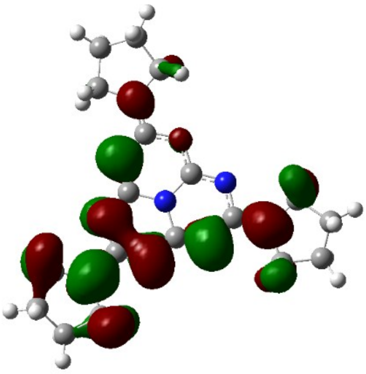
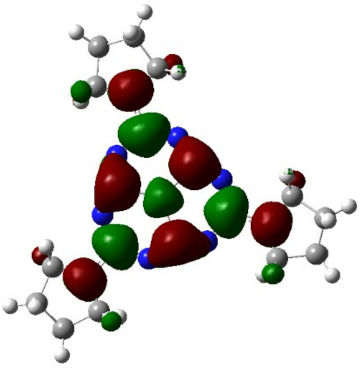
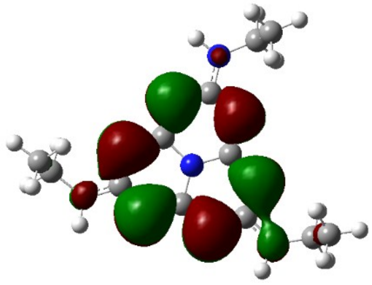
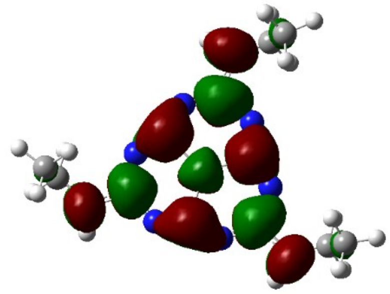
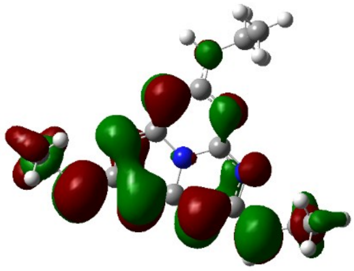
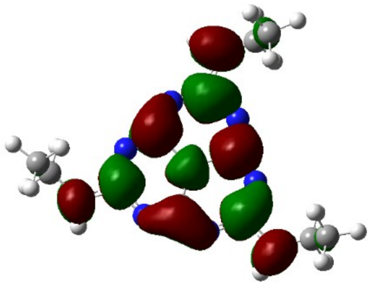
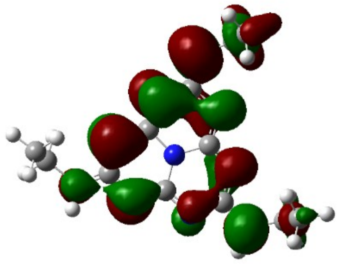
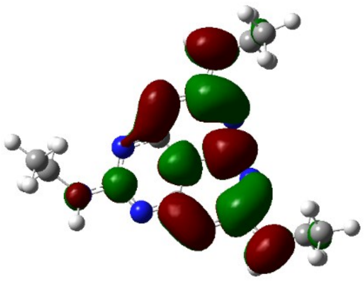
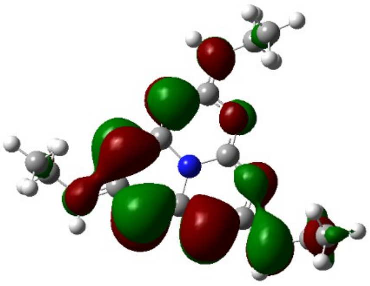
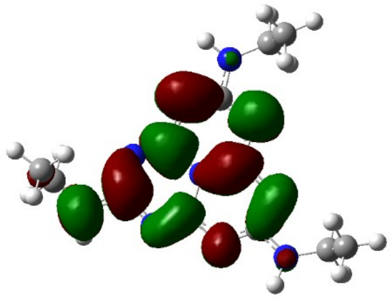
Compound	Excited state	NTO hole	NTO electron
2c	1 308 nm f=0		
2c	2 272.36 nm f=0.5043		
2c	3 273.35 nm f=0.5045		

Table S6: vertical absorption transitions computed by TD-DFT and corresponding Natural Transition Orbitals for heptazine **2c**.

Compound	Excited	NTO hole	NTO electron

	state		
2’	1[a] 308 nm f=0.001	 HOMO	 LU MO
2’	2 261 nm f=0.337		
2’	3 257 nm f=0.093		
2’	4 255 nm f=0.350		

[a] this transition implies only one orbital for the hole and one for the electron so NTO analysis was not necessary.

Table S7: vertical absorption transitions computed by TD-DFT and corresponding Natural Transition Orbitals for heptazine **2’**.

Compound	Excited state	NTO hole	NTO electron

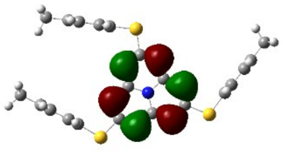
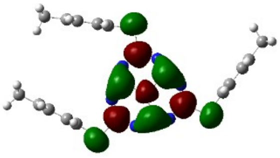
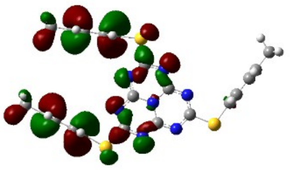
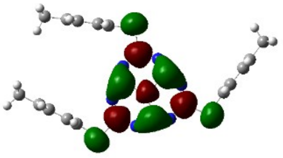
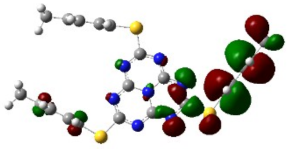
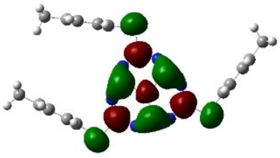
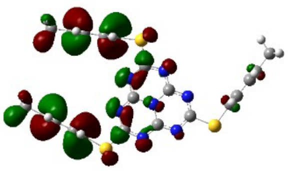
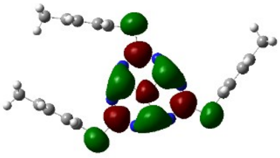
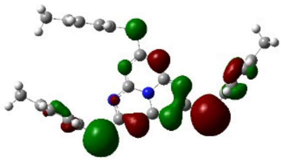
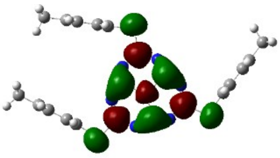
3’	1 374 nm f=0.0016		
3’	2 336 nm f=0.0000		
3’	3 334 nm f=0.0001		
3’	4 331 nm f=0.0000		
3’	5 318 nm f=0.5827		

Table S8: vertical absorption transitions computed by TD-DFT and corresponding Natural Transition Orbitals for heptazine **3’**.

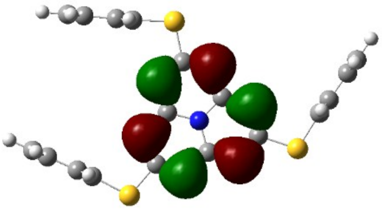
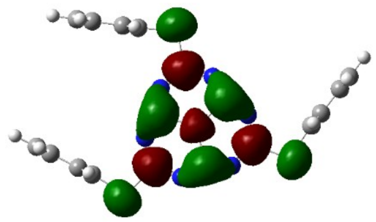
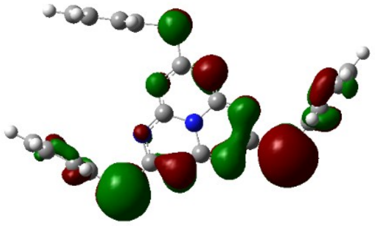
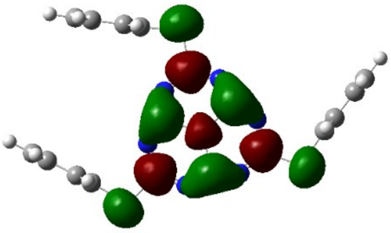
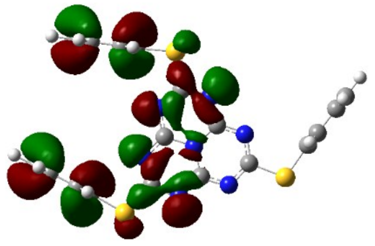
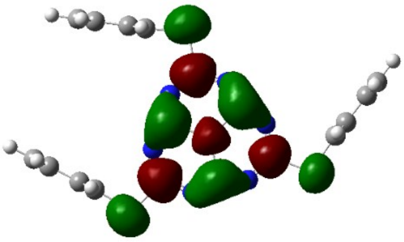
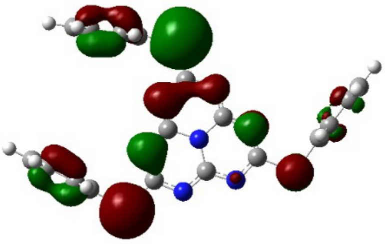
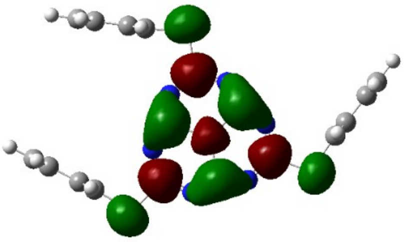
Compound	Excited state	NTO hole	NTO electron
3b	1 374 nm f=0.0015		
3b	2 316.7 nm f=0.553		
3b	3 316.5 nm f=0.0051		
3b	4 314.6 nm f=0.3249		

Table S9: vertical absorption transitions computed by TD-DFT and corresponding Natural Transition Orbitals for heptazine **3b**

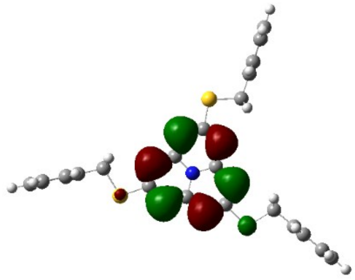
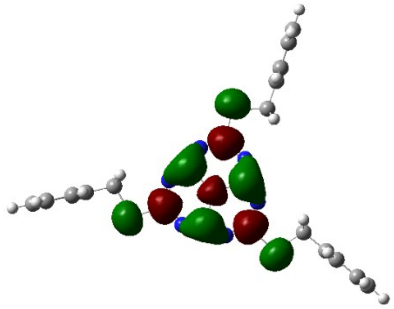
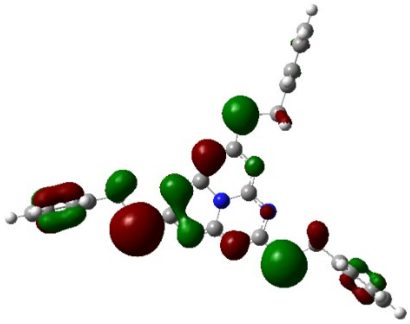
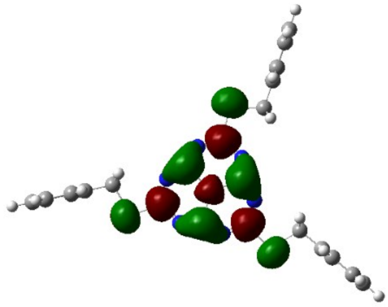
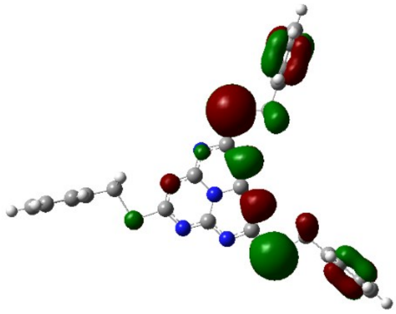
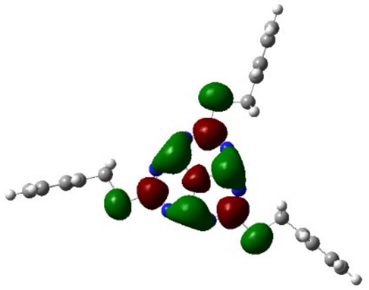
Compound	Excited state	NTO hole	NTO electron
3c	1 373 nm f=0.0016		
3c	2 330 nm f=0.5785		
3c	3 324 nm f=0.4580		

Table S10: vertical absorption transitions computed by TD-DFT and corresponding Natural Transition Orbitals for heptazine **3c.**

	S1 level /nm	Tn level /nm	T1 level / nm	Δ E S1-T1(cm-1)	Δ E S1-Tn(cm-1)
1	375.2	376.2	397.1	1470	71
2a	307.9	314.4	330.8	2248	671
2b	305.9	306.6	333.1	2669	75
2c	308.5	315.3	330.9	2194	699
2d	307.8	315.6	317.5	993	803
3a	373.7	391.2	391.2	1197	1197
3b	373.9	391.6	391.6	1209	1209
3c	373.2	377.3	393.9	1408	291

Table S11: singlet and triplet energy level computed at the TD-DFT level (B3LYP 311G+(d,p)). S1 and T1 are the lowest singlet and triplet levels, Tn is the triplet level closest in energy to S1.

7. References

[1] T. Saplinova, V. Bakumov, T. Gmeiner, J. Wagler, M. Schwarz, E. Kroke, *Z. Anorg. Allg. Chem.* **2009**, NA-NA.

[2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, B. G. J. J. Bloino, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallington CT, **2009**.