

Synthesis of linear and hyperbranched tetrazine-based polyheterarylene assemblies with high nitrogen content

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Received 21 June 2007; revised 24 July 2007; accepted 26 July 2007

Available online 1 August 2007

Abstract—The synthesis of polyheterarylenes containing exclusively *s*-tetrazine and another nitrogen heterocycle (pyridine or *s*-triazine) is described. The key step involved the polymerization of a suitable di- or triamidrazone, leading to a linear or hyperbranched dihydrotetrazine-based assembly, respectively. The triazinylenetetrazinylene material stands as one of the most nitrogenated polymers ever described.

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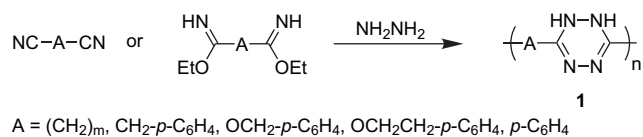
1. Introduction

Poly(azahetarylene)s have been the subject of numerous studies, particularly owing to their luminescent and electron transport properties.^{1–3} Polypyridine⁴ is a reference compound of this class, but polypyrimidine⁵ and pyridine oligomers have also been described⁶ and sometimes used as complexants⁷ or as building blocks for metallocsupramolecular chemistry.⁸ The transition metal complexes of aza-heterocyclic-based molecular architectures are also widely known as luminescent and redox-active materials.⁹

Due to the large scope of applications of tetrazine-based compounds,¹⁰ the introduction of tetrazine units would give such materials new valuable properties. As a matter of fact, tetrazines exhibit dye,¹¹ insecticide,¹² optical,^{13,14} electrochemical,¹⁵ biomedical^{16,17} properties, and readily react in inverse demand Diels–Alder reactions.¹⁸ Some tetrazine compounds are also known for their use in explosives and propellants.¹⁹ Focusing on the latter feature, our aim was to synthesize polymers with a high nitrogen content, in order to optimize their use as energetic components. Indeed, the high density, heat of formation and thermal stability of high-nitrogen compounds make them attractive materials as pyrotechnic fuels²⁰ or gas generators.²¹ In this paper, we will describe our efforts towards the synthesis of unprecedented all-heterocyclic, tetrazine-based architectures. Two structures were addressed: (i) a polymer bearing an *s*-tetrazine ring directly connected

to a pyridine ring and (ii) a hyperbranched assembly of *s*-tetrazine and *s*-triazine units. Such polymers could benefit from several advantages over monomeric compounds, including long-term stability and chemical resistance. Moreover, these targets should exhibit modular solubilities, ranging from soluble (linear oligomers) for use as energetic binders to insoluble (hyperbranched polymer) for specific applications.

In the literature, only a few tetrazine-containing polymers have been mentioned.²² One of the known pathways towards tetrazine polymers arises from the well-known reaction of hydrazine with nitriles to build the dihydrotetrazine ring.²³ This has been used with polyacrylonitrile as a starting material.^{22c} However, the incorporation of tetrazine rings remained weak by this method and it was not clear whether tetrazine or aminotriazole was the actual pendant nucleus formed during the process. More than 30 years ago, Romanian and Japanese authors demonstrated the synthesis of polymers containing tetrazine rings in the main chain.^{22d–f} The key step was the polycondensation of a dinitrile or of the corresponding diimidate with hydrazine to obtain a polydihydrotetrazine polymer of type **1** (Scheme 1). Even though this reaction was restricted to non-heterocyclic precursors, we anticipated that this polycondensation strategy could be extended further in order to synthesize our target architectures.



Scheme 1. Polycondensates containing a dihydrotetrazine ring (Refs. 22d–f).

Keywords: Nitrogen heterocycles; Tetrazine; Polymerization; Microwaves.
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2. Results and discussion

2.1. Linear polymer **5** constituted of *s*-tetrazine and pyridine units

The synthesis of **5** is outlined in Scheme 2.

Following the work of Korshak et al.,²⁴ pyridine-2,6-diimide dihydrochloride was synthesized by bubbling gaseous HCl into a dioxane solution of pyridine-2,6-dicarbonitrile containing ethanol. The isolated crude dihydrochloride was not suitable for polycondensation due to low purity. Instead the free diimide **2** was obtained in pure form in a 46% yield after neutralization of this crude product with saturated aqueous sodium carbonate. The reaction with hydrazine hydrate (proposed by Stoicescu-Crivetz et al.^{22d,e}) was used in a second step to produce the poly(2,6-pyridinediyl-dihydro-*s*-tetrazinylene). As a result, we did not observe the formation of the polymer but diamidrazone **3** quickly separated from the reaction mixture and was isolated in high yield. It is likely that the insolubility of **3** in THF is responsible for the ineffective polycondensation reaction. Further attempts to produce the polymer from **3** in DMF (in which it was found sparingly soluble) using classical heating conditions failed. Activation of the polycondensation step by microwave irradiation was then investigated. A first experiment, using an irradiation power of 50 W and DMF as solvent, yielded after precipitation in MeOH a yellow solid, which turned orange upon standing in ambient air. This was attributed to a partial oxidation of the dihydro-*s*-tetrazine moieties into tetrazines. The reaction conditions were then optimized, by varying experimental parameters including irradiation power, time and temperature (Table 1).

The application of an irradiation power of 40 W at 150 °C for 20 min led to the maximum yield of 47%, this value decreasing with higher power and longer irradiation time. At 60 W, a treatment with methanol did not produce any precipitate at all, indicating a possible degradation of the polymer (entry 4). Using other similar polar solvents allowed us to

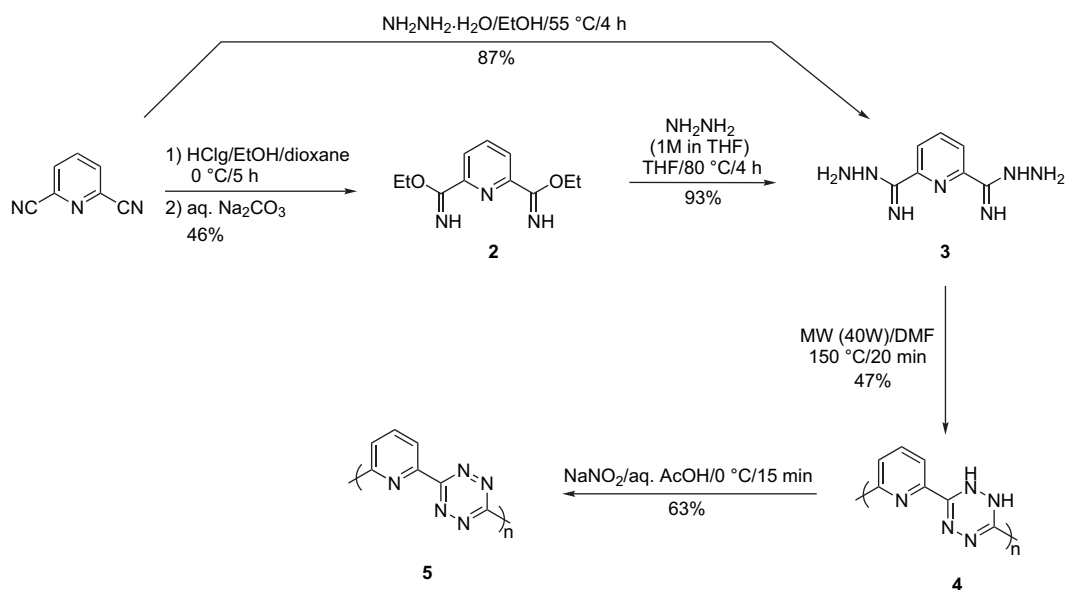
Table 1. Optimization of the polycondensation reaction leading to **4**

Entry	Solvent	Power of irradiation (W)	Temperature (°C)	Time (min)	Isolated yield ^a (%)
1	DMF	40	150	20	47
2	DMF	40	150	60	45
3	DMF	50	150	60	16
4	DMF	60	150	30	0
5	DMSO	50	180	20	40
6	NMP	50	195	20	42

^a Weight of polymer **4**/weight of **3**.

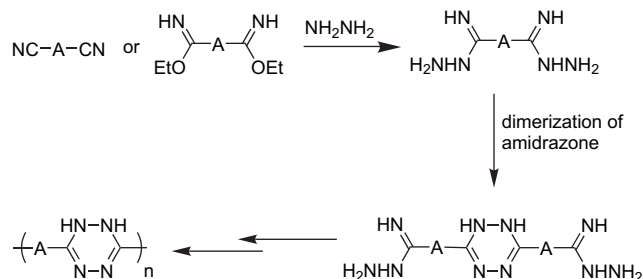
work at higher temperatures, however, yields were slightly lower than in DMF (entries 5 and 6). The high resolution ¹³C and ¹⁵N solid state NMR spectra of **4** showed the expected lines for the polymer structure, especially regarding the dihydro-*s*-tetrazine moiety. An extra signal representing a minor contribution (see Section 4) was also observed in the ¹⁵N spectrum at –310 ppm, indicative of an NH₂ group, which was assigned to a partial rearrangement of the dihydro-*s*-tetrazine moiety to a 4-amino-1,2,4-triazole moiety. This is a known process²⁵ that was further evidenced in recent microwave experiments.²⁶ Actually, elemental analyses revealed the presence of oxygen due to water inclusion, as already observed for polypyrimidine.⁵ Steric exclusion chromatographic analysis could not be performed due to the high insolubility of **4**.

Having established that pyridine-2,6-diamidrazone **3** would be a more useful intermediate than the corresponding diimide dihydrochloride, the known²⁷ **3** was synthesized directly from pyridine-2,6-dicarbonitrile. The reaction with hydrazine hydrate produced the expected diamidrazone in good yield and purity. However, the microwave treatment led to the polycondensate **4** with only a 10% yield. This drop in yield when changing the conditions of synthesis of the diamidrazone is still unexplained, since ¹H NMR spectra and elemental analyses were very similar regardless of the origin of the diamidrazone. A probable reason could be the generation of a side product in minute amount, which would interfere with the polycondensation process. From a



Scheme 2. Synthesis of polymer **5**.

mechanistic point of view, these results clearly evidenced that a diamidrazone is the key intermediate in the process of hydrazine-mediated polycondensation of diimides to polydihydrotriazines (Scheme 3), as anticipated from the known dimerization of amidrazones.²³

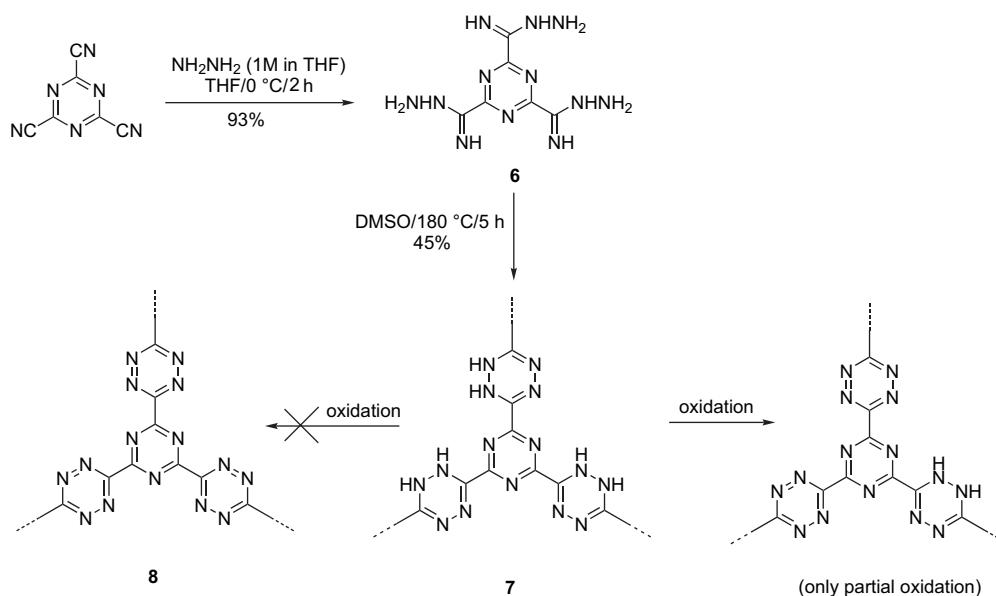


Scheme 3. Mechanism of hydrazine-mediated polycondensation of diimides or diimides to polydihydrotriazines.

The poly(2,6-pyridinediyl-dihydro-*s*-tetrazinylene) **4** was subjected to the usual sodium nitrite/aq AcOH oxidation conditions.²⁸ The suspension immediately turned to pink, while a red solid separated. The oxidation of the tetrazine nucleus was confirmed, in the ¹⁵N CP/MAS spectrum, by both the presence of a new signal at 8 ppm (tetrazine nitrogen) and the disappearance of the NH signal at -250 ppm. As for **4**, elemental analyses of the tetrazine polymer **5** showed the presence of oxygen, which was attributed to the hygroscopic character of the product. This was confirmed by the loss of the large absorption band centred at 3300 cm⁻¹ in the IR spectrum (assigned to OH bonds) when the sample was dried at 80 °C in vacuum. This signal reappeared within a few minutes upon air exposure.

2.2. Hyperbranched polymer **8** consisting of *s*-tetrazine and *s*-triazine units

The synthesis of **8** is outlined in Scheme 4.



Scheme 4. Synthesis of polymer **8**.

The successful synthesis of the pyridyltetrazine-based polymer prompted us to challenge an ever more nitrogenated structure, consisting of alternating 1,3,5-triazine and 1,2,4,5-tetrazine rings. The known^{29–31} 2,4,6-tricyano-1,3,5-triazine (TCT) was used as the starting material to achieve this goal, using the general methodology described above for polymer **5**. TCT was prepared using a modification of the patent of Beck,³⁰ using strictly anhydrous conditions in order to limit hydrolysis of TCT to hydroxydicyano-*s*-triazine.³¹ The synthesis of the corresponding imidate was attempted using the HCl_g/EtOH method, nevertheless the hydrochloride was found to be very prone to hydrolysis. The triamidrazone was therefore directly synthesized from TCT with hydrazine (1 M in THF) yielding an orange solid. Although its high insolubility made purification and characterization difficult, this new product was identified as the wanted *s*-triazine-triamidrazone by ¹³C and ¹⁵N solid state CP/MAS NMR, elemental and IR analyses.

The polycondensation could be carried out using classical experimental conditions in DMSO at high temperature leading to an optimal yield of 44%. This implies that the *s*-triazine-triamidrazone is more reactive than the related pyridine-2,6-diamidrazone, certainly resulting from the more pronounced electron-deficient character of the triazine nucleus. The use of microwave irradiation was also investigated but did not yield any improvement. The highly insoluble material was analyzed by ¹³C and ¹⁵N CP/MAS NMR spectroscopies. The expected lines for structure **7** were observed, but were also accompanied by an extra NH₂ signal (shoulder at -310 ppm) assigned to a partial rearrangement of dihydrotriazine moieties into 4-amino-1,2,4-triazole units. This product was found hygroscopic, the elemental composition being consistent with two water molecules per unit.

Polymer **7** stands as one of the most nitrogenated polymers described (theoretical N content: 62.7%), comparing well with other high-nitrogen polymers³² based on triazine^{33–35}

or tetrazole³⁶ monomers. A density of 1.56 was measured for **7**, a value, which is significantly higher than the one reported for amorphous poly(*p*-phenylene) (1.11³⁷). This clearly shows how the introduction of nitrogen heterocycles in polyarylene structures is valuable in the field of energetic materials, by increasing this crucial parameter.

The NaNO₂/aq AcOH oxidation method was ineffective in the case of polymer **7**, presumably for insolubility reasons. Several other oxidants were tested without success except N₂O₄.³⁸ Liquid N₂O₄ was introduced directly in a small reactor containing the solid dihydrotetrazine polymer **7**. After elimination of the excess N₂O₄ under a nitrogen stream, the resulting solid was analyzed by ¹³C and ¹⁵N solid state CP/MAS NMR. New lines assignable to the expected tetrazine polymer were observed (especially at –5 and –239 ppm in the ¹⁵N spectrum), however, remaining contributions from dihydrotetrazine moieties were still detected even after using harsh oxidation conditions (excess N₂O₄, 6 h at 15 °C). Presumably, the highly reticulated structure of **7** generates inaccessible sites for the oxidant, leading to a structure constituted of both dihydrotetrazine and tetrazine moieties.

3. Conclusion

In this work, original molecular architectures have been described, constituted exclusively of aza-heterocycles: (dihydro)-*s*-tetrazine and pyridine or *s*-triazine. In the pyridine series, we showed that pyridine-2,6-diamidrazone can be converted in two steps into a polymer bearing alternating pyridine and tetrazine units. The key polycondensation step to the dihydrotetrazine polymer was achieved using microwave activation. These results are in contrast with already published syntheses of tetrazine polymers containing aliphatic and/or phenyl residues. In those cases, polymers were obtained directly from the reaction of hydrazine with dinitriles or diimidates. Present results clearly established that the diamidrazone is the actual intermediate in the polymerization process.

In the *s*-triazine series, microwave activation was useless to obtain the hyperbranched dihydrotetrazine polymer **7**. This product exhibits a high nitrogen content, comparing well with the reference nitrogenated polymers from the literature. Nevertheless the final oxidation step was incomplete, leaving a polymer containing both dihydro-*s*-tetrazine and *s*-tetrazine moieties. These all-aza-heterocyclic assemblies containing tetrazine units could be of great interest in many fields, taking advantage of the unique properties of the tetrazine nucleus. In particular, the high density of **7** makes it a potential candidate in energetic applications.

4. Experimental

4.1. General

Solutions in (CD₃)₂SO, with concentrations in the range of 30–100 mg/mL were prepared for solution-state NMR analyses. All NMR measurements were performed at room temperature on Bruker Avance 200, Avance 300 WB and Avance 400 WB spectrometers. For solution-state experiments, we

used a standard Bruker 5 mm QNP probe for ¹H measurements and an H-X broadband probe for 10 mm sample tubes for ¹³C and ¹⁵N measurements. ¹H and ¹³C chemical shifts were calibrated according to DMSO signal (¹H: 2.5 ppm; ¹³C: 39.5 ppm) or acetone signal (¹H: 2.05 ppm; ¹³C: 29.92 ppm with respect to TMS, 0 ppm) used as secondary internal references. The ¹⁵N signal of a 90% formamide solution in DMSO (–269.5 ppm with respect to CH₃NO₂, 0 ppm) was used as an external secondary reference for ¹⁵N chemical shifts. High resolution solid state spectra were acquired with a Bruker broadband X-H CP/MAS probe (7 and 4 mm outer diameter rotors). Using the CP/MAS (Cross-Polarization/Magic Angle Spinning) experiment the intensity of the NMR lines is primarily related to the efficiency of the cross-polarization transfer, which depends on the number of hydrogen atoms and their distance from nitrogen. Hence, amine protons appeared more intense than ring pyridine-like nitrogen atoms. ¹H, ¹³C and ¹⁵N chemical shifts were calibrated according to external secondary references: water (4.8 ppm with respect to TMS, 0 ppm), adamantane (up-field ¹³C transition at 38.46 ppm with respect to TMS, 0 ppm) and NH₄NO₃ (down-field transition at –358.4 ppm with respect to CH₃NO₂, 0 ppm). For a more detailed description of NMR experimental conditions and assignments of products **3–7**, see also Ref. 39. Multiplicity is indicated using the following abbreviations: d for a doublet, t for a triplet, q for a quadruplet, and br s for a broad singlet. Infrared spectra were recorded with an attenuated total reflectance Perkin–Elmer SpectrumOne spectrometer. Melting points were determined on a Kofler apparatus and are uncorrected. Elemental analyses were performed on a ThermoFisher Scientific Flash EA 1112CHNS/O apparatus. Microwave-assisted reactions were performed with a CEM Discover apparatus. Reagent-grade dioxane and THF were distilled from sodium–benzophenone ketyl. Acetonitrile was distilled over CaH₂. Anhydrous ethanol was obtained by distillation over magnesium ethoxide. All other reagents were purchased from Sigma–Aldrich and were used as such.

4.2. Pyridine-2,6-diimidate **2**

Gaseous HCl was bubbled at 0 °C over 5 h in a solution of pyridine-2,6-dicarbonitrile (2 g, 15.5 mmol) in freshly distilled dioxane (40 mL) containing anhydrous ethanol (2.3 mL, 40 mmol). The reaction mixture was stored at 5 °C for 3 days. The white solid was then filtered and washed with diethylether. The resulting crude dihydrochloride was dissolved in water and neutralized by adding saturated aqueous Na₂CO₃. The precipitate was filtered and washed with water to give pure **2** as a white solid, mp 72 °C. Yield 1.47 g (46%). IR: ν =3261, 3239, 2979, 2934, 2899, 1660 cm^{–1}. ¹H NMR (200 MHz, DMSO-*d*₆, 21 °C): δ =8.13 (t, ³J_{H,H}=7.2 Hz, 1H, 4-H), 7.95 (d, ³J_{H,H}=7.5 Hz, 2H, 3-H+5-H), 4.34 (q, ³J_{H,H}=7.0 Hz, 2H, CH₂), 1.36 (t, ³J_{H,H}=7.0 Hz, 3H, CH₃) ppm. ¹³C NMR (50 MHz, DMSO-*d*₆, 21 °C): δ =163.6, 146.6, 140.0, 122.3, 61.7, 14.1 ppm. Anal. Calcd for C₁₁H₁₅O₂N₃: C 59.71, H 6.83, N 18.99. Found: C 59.53, H 6.79, N 18.53.

4.3. Pyridine-2,6-diamidrazone **3**

This product was obtained from pyridine-2,6-dicarbonitrile as described,²⁷ or from diimidate **2**: pyridine-2,6-diimidate

2 (0.9 g, 4.1 mmol) was dissolved in hydrazine (1 M in THF, 16 mL, 16 mmol) and the reaction mixture was heated at 80 °C for 4 h. The precipitate was filtered and washed with THF to give **3** as a yellow solid. Yield 0.73 g (93%). IR: $\nu=3450, 3292, 3190, 1664, 1621, 1585, 1568, 1460, 1425 \text{ cm}^{-1}$. ^1H NMR (200 MHz, DMSO- d_6 , 21 °C): $\delta=7.82$ (d, $^3J_{\text{H,H}}=7.1$ Hz, 2H, 3-H+5-H), 7.64 (m, 1H, 4-H), 6.05 (br s, 4H), 5.25 (br s, 4H) ppm. ^{13}C NMR (50 MHz, DMSO- d_6 , 21 °C): $\delta=150.2, 143.6, 136.0, 118.0$ ppm. ^{15}N NMR (30 MHz, DMSO- d_6 , 21 °C): $\delta=-97.7, -130.2, -287.1, -320.4$ ppm.

4.4. Poly(2,6-pyridinediyl-dihydro-s-tetrazinylene) **4**

A suspension of diamidrazone **3** in the appropriate solvent (100 g/L) was heated under microwave irradiation for specified time (see Table 1). After cooling, the polymer was precipitated by adding methanol into the reaction mixture. The solid was filtered and washed with methanol to give **4** as a yellow solid. Optimal conditions: DMF, 40 W, 150 °C, 20 min. Yield 46%. IR: $\nu=3335, 1615, 1584, 1560, 1461, 1387 \text{ cm}^{-1}$. ^{13}C solid state NMR (100 MHz, 21 °C): $\delta=150.2, 146.3, 137.4, 122.4$ ppm. ^{15}N solid state NMR (40 MHz, 21 °C): $\delta=-94, -118, -254$ ppm. Anal. Calcd for $(\text{C}_7\text{H}_5\text{N}_5 \cdot 0.3\text{H}_2\text{O})_n$: C 51.09, H 3.43, N 42.56. Found: C 51.61, H 3.85, N 40.51 (the nitrogen content was consistently lower than expected; this had been observed before in other tetrazine-based compounds^{19c}).

4.5. Poly(2,6-pyridinediyl-s-tetrazinylene) **5**

Saturated aqueous NaNO₂ was added dropwise at 0 °C into a solution of polydihydro-tetrazine **4** (93 mg) in water/acetic acid 1:3 (6 mL). The pink reaction mixture was neutralized with 30% aqueous ammonium hydroxide and filtered. The solid was placed in a Soxhlet apparatus and extracted with water (24 h) and then with acetone (24 h) to give **5** as a red solid. Yield 58 mg (63%). IR: $\nu=3350, 1614, 1440, 922 \text{ cm}^{-1}$. ^{13}C solid state NMR (75 MHz, 21 °C): $\delta=162.4, 148.4, 140.7, 125.8$ ppm. ^{15}N solid state NMR (30 MHz, 21 °C): $\delta=8, -170$ ppm. Anal. Calcd for $(\text{C}_7\text{H}_3\text{N}_5 \cdot 0.6\text{H}_2\text{O})_n$: C 50.06, H 2.52, N 41.70. Found: C 50.07, H 3.06, N 38.47 (the nitrogen content was consistently lower than expected; this had been observed before in other tetrazine-based compounds^{19c}).

4.6. 2,4,6-Tricyano-1,3,5-triazine

Calcined sodium cyanide was introduced under argon in a 500 mL three-necked flask, followed by the addition of dry acetonitrile (300 mL). The mixture was cooled to -35 °C and 2,4,6-trifluoro-1,3,5-triazine (12.7 mL, 0.148 mol) was added dropwise. The reaction mixture was warmed to 0 °C and stirred at 0 °C for 8 h, and then at 15 °C for 13 h. The dark brown reaction mixture was filtered and the filtrate evaporated. The resulting red solid was extracted with anhydrous dichloromethane for 4 h at room temperature. The mixture was filtrated and the filtrate evaporated. The resulting brown solid was purified by sublimation (85 °C at 5×10^{-4} mbar). The 2,4,6-tricyano-1,3,5-triazine was obtained as a white solid, mp 120 °C. Yield: 10.62 g (46%). IR: $\nu=2276, 2255, 1510, 1333, 937, 819 \text{ cm}^{-1}$. ^{13}C NMR (200 MHz, acetone- d_6 , 21 °C): $\delta=155.1, 113.7$ ppm.

Anal. Calcd for C₆N₆: C 46.16, N 53.84. Found: C 45.90, N 53.69.

4.7. s-Triazine-triamidrazone **6**

2,4,6-Tricyano-1,3,5-triazine (700 mg, 4.49 mmol) was introduced in a 50 mL three-necked flask and anhydrous THF (5 mL) was added under nitrogen. The mixture was cooled to 0 °C and hydrazine (1 M in THF, 35 mL, 35 mmol) was added dropwise. An orange precipitate separated. The reaction mixture was stirred for 2 h at 0 °C, then filtrated and washed with hot THF to give **6** as an orange solid. Yield: 1.05 g (93%). IR: $\nu=3421, 3299, 3183, 1653, 1620, 1538, 1343 \text{ cm}^{-1}$. ^{13}C solid state NMR (100 MHz, 21 °C): $\delta=166.3, 146.8$ ppm. ^{15}N solid state NMR (40 MHz, 21 °C): $\delta=-132, -181, -272, -285, -325$ ppm. Anal. Calcd for C₆H₁₂N₁₂: C 28.57, H 4.79, N 66.63. Found: C 26.92, H 4.41, N 66.67.

4.8. Hyperbranched polydihydro-tetrazine **7**

Triamidrazone **6** (1.2 g, 4.7 mmol) was heated in DMSO (12 mL) at 180 °C for 5 h. The precipitate was filtered and placed in a Soxhlet apparatus. The solid was extracted with acetone for 24 h and dried in vacuo to give **7** as a brownish powder. Yield: 540 mg (45%). IR: $\nu=3202, 1698, 1625, 1532, 1369 \text{ cm}^{-1}$. ^{13}C solid state NMR (100 MHz, 21 °C): $\delta=166, 156$ ppm. ^{15}N solid state NMR (40 MHz, 21 °C): $\delta=-150 \rightarrow -180, -268$ ppm. Anal. Calcd for $(\text{C}_6\text{H}_3\text{N}_9 \cdot 2\text{H}_2\text{O})_n$: C 30.38, H 2.97, N 53.15. Found: C 30.61, H 3.00, N 53.39.

Acknowledgements

The SPOT laboratory (University of Tours) is acknowledged for microwave experiments in the triazinyltetrazine series.

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