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Synthesis of polyphilic hexaazatrinaphthylenes and mesomorphic properties

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ABSTRACT

Methodologies for the synthesis of polyphilic hexaazatrinaphthylenes (**HATN**) with reduced symmetry based on the sequential condensation reactions of 1,2-bisalkoxy-4,5-diaminobenzenes with either tetrahydroxy-1,4-quinone or hexaketocyclohexane are described. The synthesized **HATN** possesses improved mesogenic properties and is liquid crystalline at room temperature.

1. Introduction

The n-type mesogens are scarce, and acceptor materials with high charge mobility are in demand. Recently, the electron-deficient pyrazine ring system has been used in the design and synthesis of n-type material.[1–16] Hexaazatriphenylenes (**HAT**) and hexaazatrinaphthylenes (**HATN**) having three π-deficient pyrazine nuclei are strong electron acceptors that contain three bidentate binding sites, and have been studied in the context of supramolecular chemistry[17] and photo-chemistry.[18] **HAT** and **HATN** derivatives in their mesophase can self-assemble into one-dimensional column that possesses high charge carrier mobility, useful as potential n-type functional materials for practical application in nanotechnology.

In general, a wide range of variations of the peripheral side chains on the discotic mesogens have also been carried out to control the phase behavior and transition temperature, and more importantly to ensure long range ordering at the mesophase.[19–23] Recently our laboratory has developed simple efficient synthetic methodologies toward **HATN** structure of Model-**A**, and **HAT** structure of Model-**B′**, as shown in Fig. 1.[4,5,24] Most reports have been confined to symmetrically substituted **HATN** based on Model-**A** that differs only in their mono-functional group, but not the substitution patterns.[3,10–13] Discogen that possess separate structural regions can be termed polyphilic, and that the combination of hydrophilic and hydrophobic1regions is described as being amphiphilic in nature. During packing to mesophase, polyphilic disc play an important role during mesogenic self- assembly, whereby like-chemical regions tend to match, and can give rise to interesting new liquid crystalline properties. The synthesis of polyphilic **HATN** of structures **B**, **C**, and **D** (Fig. 1), has until today eluded chemists. In this paper we report practical synthetic methods for the synthesis of **HATN** polyphilic structures **C** and **D** with the hope to improve the liquid crystalline properties.

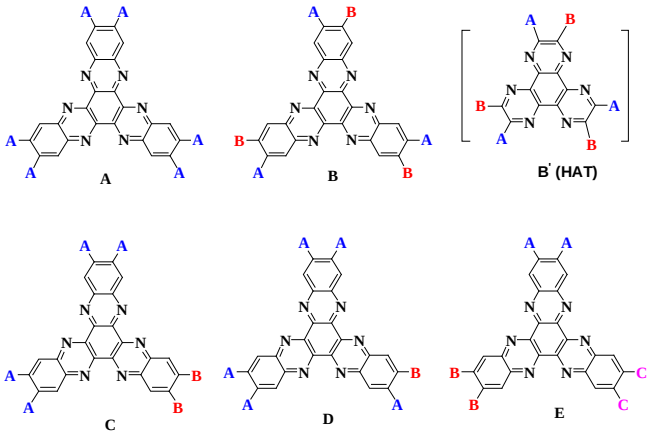

Fig. 1. The various possible substitution patterns for the **HATN** structure **A**–**E**.

2. Results and discussion

It has been reported that condensation of tetrahydroxy-1,4-quinone **1** with 1,2-diaminobenzene **2** gave 1,2,3,4-tetrahydroxy-phenazine **3**, and this can be subsequently oxidized to the

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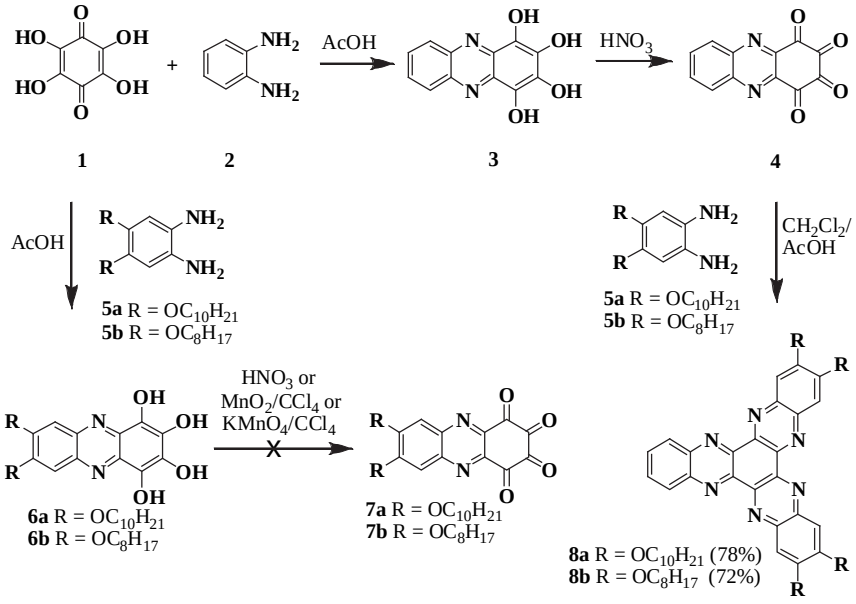
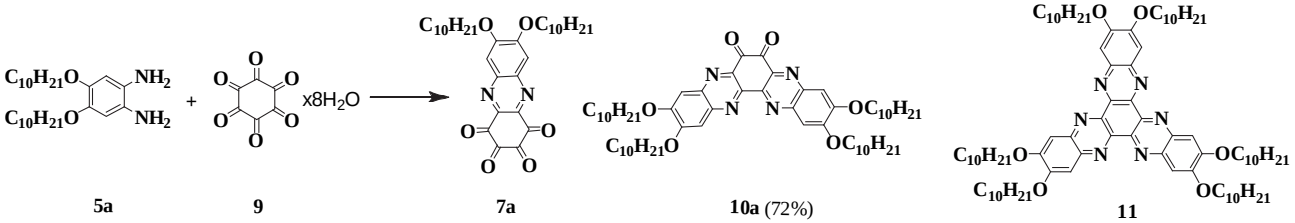
corresponding phenazinetetrone **4** (Scheme 1).[25] The condensation of 4,5-bis(alkoxy)benzene-1,2-diamine **5a** and **5b**[4,5] with tetrahydroxy-1,4-quinone **1** also gave **6a** and **6b**, but unfortunately these cannot be oxidized smoothly to **7a** and **7b** using concentrated nitric acid under the reported condition. All attempts to improve the oxidation of **6a** and **6b** under other oxidative conditions did not give the requisite **7a** and **7b** smoothly. Since we were able to obtain the reported unsubstituted phenazinetetrone **4**, this was further condensed with the prepared 4,5-bis(alkoxy)benzene-1,2-diamine **5a** and **5b** to give the tetraalkoxy-**HATN**s **8a** and **8b**. We then examined the liquid crystalline properties of **8a** and **8b** using polarized optical microscope (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). These compounds do not show liquid crystalline properties. This clearly illustrates the need of six alkoxy groups to enforce the staking of the electron-deficient **HATN** core to form mesophase.

To the best of our knowledge, there have been no reported methods for controlling the mono- or di-condensation of **5** with hexaketocyclohexane **9** for the direct preparation of the (bisalkoxy)-tetraketo-**7** and (tetraalkoxy)-diketo-**10**, respectively.[26] With the ultimate goal of synthesizing polyphilic **HATN**s, it becomes desirable to develop new expedient methodologies for their direct synthesis. At the onset, we were uncertain as to whether selective mono-condensation can be carried out successfully. The direct condensation of hexaketocyclohexane **9** with 1 equiv of **5a** in CH_2Cl_2/AcOH at room temperature for 2.5 h did not give the mono-condensation product **7a**. Instead, the tri-condensation product **11** was obtained, together with recovered starting material (Table 1, entry 1). We attributed the formation of **11** to the increasing solubility of the mono- and di-condensation products **7a** and **10a**, which undergoes condensation more rapidly as compared to **9**. Next, we first reacted **9** with 2 equiv of ethylenediamine in AcOH (5 mL) at room tempera-



Scheme 1. Synthesis of phenazine 1,2,3,4-tetraones using tetrahydroxy-1,4-quinone **1**.

Table 1
The conditions and results for condensation reaction of **9** with **5a**



Entry	**5a**:**9** (equiv)	Solvent	Time[a] (h)	Ligand	Compd[b]
1	1:1	CH_2Cl_2/AcOH	2.5		**5a**:**11** (5:1)
2	1:1	CH_2Cl_2/AcOH	2.5	Ethylenediamine 2 equiv	**5a**:**11** (10:1)
3	1:1	AcOH	2.5		**10a**:**11** (1:1)
4	1:1	AcOH	2.5	Ethylenediamine 2 equiv	**11**
5	1:1	HCOOH	2.5		**10a** (52%)[c]
6	1:1	HCOOH	2.5	Ethylenediamine 2 equiv	**10a** (61%)[c]
7	2:1	HCOOH	2.5		**10a** (72%)
8	3:1	HCOOH	2.5		**10a** (72%)

[a] All reactions were conducted at room temperature.
[b] The data of entries 1–3 were obtained from the intergration of ^{1}H NMR spectra of the unpurified products, the entries 5–8 were isolated yield.
[c] Yield based on **5a**.

ture with the hope of protecting four of the carbonyl groups, followed by the addition of 1 equiv of **5a** in CH_2Cl_2 (10 mL) for the subsequent selective mono-condensation reaction. Unfortunately, addition of the ethylenediamine failed to give the desired control for the selective synthesis of **7a** (Table 1, entry 2). The use of prolong reaction lead to an increase formation of **5a**. From our previous experience in the synthesis of **HATN**s, it is apparent that the appropriate choice of solvent is critical for controlling the course of the condensation reactions. The use of AcOH (15 mL) as solvent for the reaction of **5a** (1 equiv) with **9** was found to give the di- and tri-condensation product **10a** and **11** in a 1:1 ratio, respectively (Table 1, entry 3). Again, no mono-condensation product was observed. The reaction of **9** with 2 equiv of ethylenediamine in AcOH, followed by addition of 1 equiv of **5a** in AcOH was found to promote the formation of the tri-condensation product **11** (Table 1, entry 4). The results shown in entries 1–4 underscore the influence of solubility on the course of the reaction.

Formic acid is less hydrophobic than acetic acid. Accordingly, we choose to conduct the condensation reaction in formic acid with the hope of obtaining mono-condensation product **7a**. The reaction of 1 equiv of **5a** with **9** in formic acid (15 mL) at room temperature was found to give the di-condensation product **10a** in 52% isolated yield based on **5a** (Table 1, entry 5). Although we could not stop the reaction at the mono-condensation stage, we were delighted that we were able to obtain solely the di-condensation product for the first time. We then also reacted **9** in the presence of ethylenediamine (2 equiv) in formic acid (5 mL) at room temperature, followed by addition of 1 equiv of **5a** in formic acid (10 mL), but this also resulted in the formation of **10a** in a 61% isolated yield based on **5a** (Table 1, entry 6). In order to improve the yield, the amount of **5a** was increased to 2 equiv and **10a** can be obtained in 72% isolated yield (Table 1, entry 7). Intriguingly, **9** reacted with 3 equiv of **5a** and stopped at the di-condensation stage to give **10a** in a 72% isolated yield (Table 1, entry 8).

We have now developed the best synthetic condition for the synthesis of 2,3,10,11-tetrakis(decyloxy)quinoxalino[2,3-*a*]-phenazine-6,7-dione **10a**. Similarly, treatment of **9** with the 2 equiv of **5b**, **5c**, and **5d** in formic acid (15 mL) at room temperature gave **10b**–**d** in yields ranging between 60 and 85% (Scheme 2).

oligoether side chains, poly-**HATN-3**, also possessed good thermal stability with a low K–Col transition at 38 °C with a wide liquid crystal temperature range. The combination of the rigid cores and disordered structure of the oxygen-containing branches tails may be a driving force to the formation of a highly ordered columnar structure in the bulk state with enhanced molecular segregation. These results reflect the advantage of polyphilic **HATN** discogens for the design of low melting point discotic liquid crystals. X-ray diffraction studies of poly-**HATN-1**–**3** confirmed their columnar hexagonal mesophase assignment made by POM based on the two intense low angle peaks indexed to (100) and (110).

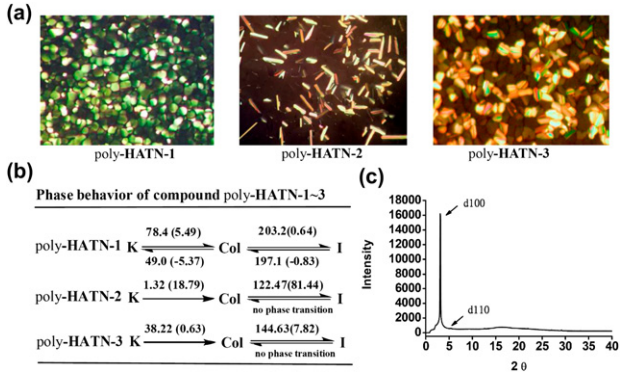
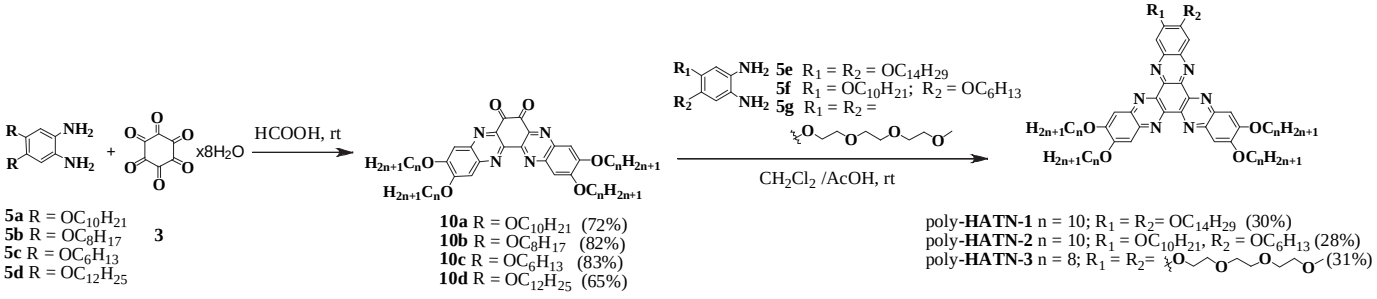


Fig. 2. (a) POM image of compound poly-**HATN-1**–**3**. (b) DSC thermographs of compound poly-**HATN-1**–**3**. The transition temperature (°C) and enthalpies (in parentheses/KJ mol^{-1}) were determined by DSC at 10 °C/min (poly-**HATN-1**) and 5 °C/min (poly-**HATN-2** and poly-**HATN-3**). K: crystalline phase; Col: columnar phase; I: isotropic phase. (c) Powder X-ray diffraction pattern of poly-**HATN-1**–**3**.

3. Conclusion

We have reported a convenient method for controlling the condensation of hexaketocyclohexane with 1,2-diaminobenzene derivatives with the choice of appropriate solvent, and this has produced mainly the di-condensation product **10** in good yield. This protocol permits the synthesis of polyphilic **HATN** of greater structural variations for the first time, which is important for the



Scheme 2. Synthesis of **10a**–**d** and 2,3,8,9-tetrakis(alkoxy)-14,15-bis(alkoxy)diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine poly-**HATN-1**–**3**.

The readily available di-condensation product **10** is now a versatile intermediate for the synthesis of polyphilic **HATN**. The condensation of **10a** with **5e** gave the budge poly-**HATN-1**. The reaction of **10a** with **5f** gave poly-**HATN-2** with further desymmetrization and such structural motif may provide further beneficial mesogenic property. Next we synthesized amphiphilic poly-**HATN-3** from the condensation of **10b** with **5g**. The mesogenic properties of poly-**HATN-1**–**3** were investigated by DSC, POM, and XRD (Fig. 2). The POM studies show that poly-**HATN-1**–**3** exhibit optical textures at the mesophase. Interestingly, poly-**HATN-2** showed a very low M–K transition at 1.32 °C in the DSC while maintaining a relatively high isotropic temperature of 122.47 °C; and more importantly remaining liquid crystalline under POM at room temperature. The generation of useful n-type functional materials. The mesophase align easily into columnar structure as observed under POM. The desymmetrization of **HATN** gave room temperature n-type discotic liquid crystal with improved processability, a useful property during fabrication on surface.

4. Experimental

4.1. General procedures and materials

^{1}H NMR spectra were measured on a 500 MHz and 200 MHz spectrometer. Natural abundance ^{13}C NMR spectra were measured using pulse Fourier transform, on a 500 MHz NMR spectrometer

operating at 125 MHz. Chemical shifts are given in parts per million (ppm) and coupling constant *J* in hertz (Hz) for both nuclei, with the solvent (usually $CDCl_3$) peak as an internal standard. The reference peak for ^{13}C is the central peak at δ 77.0. Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

*4.1.1. General procedure for the preparation of 2,3,8,9-tetrakis(alkoxy)diquinoxalino-[2,3-a:2′,3′-c]-phenazine (**8**).* To a solution of 1,2-bisalkoxy-4,5-diaminobenzene (10 mM) and phenazinetetrone (4 mM) in ethanol (10 mL) obtained after filtration of the hydrogenation reaction was added acetic acid (5 mL). The reaction mixture was refluxed under nitrogen for 24 h. Ethanol and acetic acid were then removed and the residue dissolved in dichloromethane followed by washing with $NaHCO_3$ (aq) and brine and drying over $MgSO_4$. Removal of the solvent in vacuo gave crude product that has to be rigorously purified by chromatography separation in silica gel using dichloromethane as elution and recrystallization from dichloromethane/hexane (1:1).

*4.1.2. 2,3,8,9-Tetrakis(decyloxy)diquinoxalino-[2,3-a:2′,3′-c]phenazine (**8a**).* Yellow solid (78%); ^1H NMR ($CDCl_3$, 500 MHz): δ 8.68 (d–d, *J*=3.5 Hz, 2H), 8.00 (d–d, *J*=3.5 Hz, 2H), 7.88 (s, 4H), 4.32 (t, *J*=13 Hz, 8H), 2.04–1.98 (m, 8H), 1.61–1.25 (m, 60H), 0.90 (t, *J*=14 Hz, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.04, 154.73, 143.43, 143.08, 141.80, 141.55, 141.43, 140.48, 131.30, 130.45, 107.65, 107.55, 69.63, 69.57, 31.91, 29.62, 29.57, 29.38, 29.35, 28.76, 26.05, 22.69, 14.11. LRMS (FAB): 1009.73 [$(M+H)^+$]; HRMS (FAB) calcd for $C_{64}H_{92}N_6O_4$ [$(M+H)^+$]: 1009.7180, found 1009.7189 [$(M+H)^+$].

*4.1.3. 2,3,8,9-Tetrakis(octyloxy)diquinoxalino-[2,3-a:2′,3′-c]phenazine (**8b**).* Yellow solid (72%); ^1H NMR ($CDCl_3$, 500 MHz): δ 8.68 (d–d, *J*=3.5 Hz, 2H), 8.00 (d–d, *J*=3.5 Hz, 2H), 7.87 (s, 4H), 4.32 (t, *J*=13 Hz, 8H), 2.03–1.98 (m, 8H), 1.59–1.29 (m, 44H), 0.92 (t, *J*=14 Hz, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.02, 154.72, 143.42, 143.08, 141.80, 141.545, 141.42, 140.466, 131.29, 130.44, 107.63, 107.53, 69.59, 69.56, 31.80, 29.33, 29.27, 28.76, 26.043, 22.66, 14.102. LRMS (FAB): 897.60 [$(M+H)^+$]; HRMS (FAB) calcd for $C_{56}H_{76}N_6O_4$ [$(M+H)^+$]: 897.5928, found 897.6026 [$(M+H)^+$].

*4.1.4. General procedure for the preparation of 2,3,10,11-tetrakis (alkoxy)quinoxalino[2,3a]phenazine-6,7-dione (**10**).* To a solution of hexaketocyclohexane (4 mM) in formic acid (5 mL) was stirred at room temperature, followed by addition of the 1,2-bisalkoxy-4,5-diaminobenzene (8 mM) dissolved in formic acid (10 mL). The reaction mixture was stirred for 2.5 h and the solid residue from the reaction mixture was filtered. The precipitated crude product was then dissolved in dichloromethane and the dichloromethane layer washed with water and brine. The dichloromethane extract was dried over $MgSO_4$ and evaporated. Removal of the solvent in vacuo gave crude product.

*4.1.5. 2,3,10,11-Tetrakis(decyloxy)quinoxalino-[2,3-a]phenazine-6,7-dione (**10a**).* Black solid (71.99%); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.79 (s, 2H), 7.44 (s, 2H), 4.38–4.12 (m, 8H), 2.18–1.90 (m, 8H), 1.72–1.10 (m, 56H), 1.02–0.86 (m, 12H). MS-[MALDI-TOF] *m*/*z*: 938.86 [$(M+H)^+$]; calcd for $C_{58}H_{88}N_4O_6$, 938.34 [$(M+H)^+$].

*4.1.6. 2,3,10,11-Tetrakis(octyloxy)quinoxalino-[2,3-a]phenazine-6,7-dione (**10b**).* Black solid (81.78%); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.79 (s, 2H), 7.44 (s, 2H), 4.24–4.21 (m, 8H), 1.95 (m, 8H), 1.53–1.28 (m, 40H), 0.88 (m, 12H). MS-[MALDI-TOF] *m*/*z*: 826.85 [$(M+H)^+$]; calcd for $C_{50}H_{72}N_4O_6$, 826.13 [$(M+H)^+$].

*4.1.7. 2,3,10,11-Tetrakis(hexyloxy)quinoxalino-[2,3-a]phenazine-6,7-dione (**10c**).* Black solid (83.46%); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.77 (s, 2H), 7.40 (s, 2H), 4.19 (m, 8H), 1.97–1.90 (m, 8H), 1.53–1.34 (m, 24H), 0.94–0.88 (m, 12H). MS-[MALDI-TOF] *m*/*z*: 714.56 [$(M+H)^+$]; calcd for $C_{42}H_{56}N_4O_6$, 713.92 [$(M+H)^+$].

*4.1.8. 2,3,10,11-Tetrakis(dodecyloxy)quinoxalino[2,3-a]phenazine-6,7-dione (**10d**).* Black solid (64.55%); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.80(s, 2H), 7.46 (s, 2H), 4.25–4.19 (m, 8H), 1.93 (m, 8H), 1.52–1.24 (m, 72H), 0.85–0.82 (m, 12H). MS-[MALDI-TOF] *m*/*z*: 1050.94 [$(M+H)^+$]; calcd for $C_{66}H_{104}N_4O_6$, 1050.56 [$(M+H)^+$].

*4.1.9. General procedure for the preparation of 2,3,8,9-tetrakis-(alkoxy)-14,15-bis-(alkoxy)-diquinoxalino[2,3-a:2′,3′-c]phenazine-(poly-**HATN**).* To a solution of 1,2-bisalkoxy-4,5-diaminobenzene (1.8 mM) and 2,3,10,11-tetrakis-(alkoxy)quinoxalino[2,3-*a*]phenazine-6,7-dione (1.6 mM) in dichloromethane (20 mL) obtained after filtration of the hydrogenation reaction was added acetic acid (3 mL). The reaction mixture was stirred at room temperature for 24 h. Removal of the solvent in vacuo gave crude product that has to be rigorously purified by chromatography separation in silica gel using dichloromethane as elution and recrystallization from acetone or ethanol.

*4.1.10. 2,3,8,9-Tetrakis(decyloxy)-14,15-bis-(tetradecyloxy)diquinoxalino[2,3-a:2′,3′-c]phenazine (poly-**HATN-1**).* Yellow solid (30%); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.83 (s, 6H), 4.30 (t, *J*=6.5 Hz, 12H), 1.99 (quint, *J*=7.5 Hz, 12H), 1.58 (quint, *J*=7.5 Hz, 12H), 1.68–1.04 (m, 88H), 0.91–0.87 (m, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.44, 141.24, 140.905, 107.57, 69.44, 31.89, 29.70, 29.64, 29.61, 29.61, 29.56, 29.38, 29.34, 29.33, 28.77, 26.05, 22.66, 14.09. MS-[MALDI-TOF] *m*/*z*: 1435.22 [$(M+H)^+$]; calcd for $C_{92}H_{148}N_6O_6$, 1435.20 [$(M+H)^+$].

*4.1.11. 2,3,8,9,14-Pentakis(decyloxy)-15-(hexyl-oxy)diquinoxalino [2,3-a:2′,3′-c]phenazine (poly-**HATN-2**).* Yellow solid (28%); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.76 (s, 6H), 4.25 (t, *J*=6.5 Hz, 12H), 1.96 (quint, *J*=7.5 Hz, 12H), 1.55 (quint, *J*=7.5 Hz, 12H), 1.41–1.22 (m, 64H), 0.93–0.854 (m, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.34, 141.12, 140.75, 107.45, 69.37, 31.85, 31.513, 29.57, 29.52, 29.35, 29.29, 28.74, 26.00, 25.66, 22.62, 22.55, 14.04, 14.01, 13.955. MS-[MALDI-TOF] *m*/*z*: 1265.99 [$(M+H)^+$]; calcd for $C_{80}H_{124}N_6O_6$, 1265.96 [$(M+H)^+$].

*4.1.12. 2,3-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-8,9,14,15-tetrakis(octyloxy)diquinoxalino-[2,3-a:2′,3′-c]phenazine (poly-**HATN-3**).* Yellow solid (31%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 2H), 7.84 (s, 4H), 4.44 (t, *J*=4 Hz, 4H), 4.30 (t, *J*=6.5 Hz, 8H), 4.06 (t, *J*=4.5 Hz, 4H), 3.85 (t, *J*=4.5 Hz, 4H), 3.74 (t, *J*=5 Hz, 4H), 3.70 (t, *J*=4 Hz, 4H), 3.58 (t, *J*=4.5 Hz, 4H), 3.39 (s, 6H), 2.03–1.97 (m, 8H), 1.86–1.26 (m, 40H), 0.93–0.87 (m, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.58, 154.55, 153.67, 141.39, 141.32, 141.24, 141.19, 141.12, 140.828, 107.92, 107.59, 71.94, 71.07, 70.74, 70.60, 69.50, 69.14, 68.92, 59.05, 31.81, 29.42, 29.35, 29.27, 28.77, 26.06, 22.67, 14.11. MS-[MALDI-TOF] *m*/*z*: 1221.80 [$(M+H)^+$]; calcd for $C_{70}H_{104}N_6O_{12}$, 1221.77 [$(M+H)^+$].

Acknowledgements

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Supplementary data

A PDF file containing the MALDI-TOF spectrum of compounds poly-**HATN-1**–**3**. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.09.064. These data include MOL files and InChIKeys of the most important compounds described in this article.

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