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Inherently Chiral Iminoresorcinarenes through Regioselective Unidirectional Tautomerization

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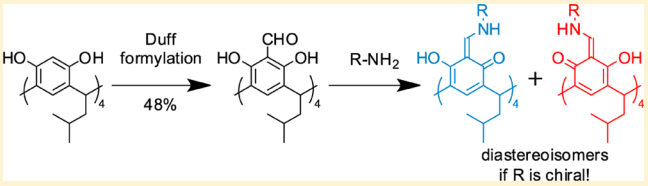
Supporting Information

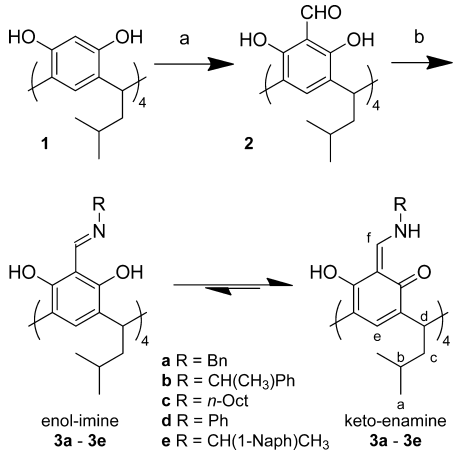
ABSTRACT: Tetraformylresorcin[4]arene is obtained in 48% yield via a chromatography-free Duff reaction. The formylated resorcinarene reacts easily with primary aliphatic and aromatic amines. The resulting imines exist exclusively in keto-enamine forms. Owing to a system of intramolecular hydrogen bonds, the reaction selectively leads to regioisomers with C_4 symmetry. They possess an inherent chirality due to a propeller-like skeleton. For chiral amines, inherently chiral diastereoisomers are observed.



Cavity-containing supramolecular structures have found numerous applications as sensors,[1] components of sorption materials,[2] supramolecular catalysts,[3] and reaction nanovessels.[4,5] Such structures are often large and highly ordered. The number of bonds that have to be formed during their synthesis and the proper spatial arrangement requires unusual precision that is rarely achievable in kinetically driven processes. Therefore, an approach based on reversible reactions is more effective. It facilitates postsynthetic error corrections and allows the most thermodynamically stable structure to be selected and amplified. For the synthesis of large, cavity-containing structures, reversibility of the formation of coordination bonds[6−9] or imine bonds[10−12] has proven to be highly beneficial. We envisioned that tetraformylresorcin[4]-arene **2**, possessing free OH groups, would be an important intermediate for the construction of supramolecular assemblies based on imine-forming reactions. The new features were expected to come from the ability of the phenolic hydroxyl group to participate in hydrogen bonding and tautomeric equilibrium (keto−enol). This may introduce directionality and cause the formation of chiral propeller-like structures. In this paper, we describe the first successful synthesis of tetraformylresorcin[4]arene **2** (unknown thus far, Scheme 1). We also prove its great potential in the formation of a new type of inherently chiral cavity-containing compounds[13] based on regioselective formation of keto−enol tautomers. Additionally, we show that such dervatives can be efficiently formed by chiral self-sorting.

Introduction of formyl functionalities into a preformed macrocyclic skeleton is often problematic. Reactions that work nicely on simple analogues do not transfer easily into macrocyclic scaffolds. For example, the very simple supramolecular building block tetraformylresorcin[4]arene **2** has not been known until now (Scheme 1). Although the synthesis of its *O*-alkylated analogue was previously reported[14−19] using tetrabromo-*O*-alkylated resorcinarene, BuLi, and DMF (or *N*-formylmorpholine), a similar procedure cannot be applied to obtain **2**. Numerous attempts have been made by many

Scheme 1. Formylation of Resorcin[4]arene and the Formation of Imines[a]



[a]Reaction conditions: (a) HMTA, TFA, see Table 1; (b) R-NH_2, $CHCl_3$.

research groups to directly formylate resorcin[4]arene **1** using other methods. The classical Reimer−Tiemann reaction ($CHCl_3$/KOH) was used with different substrate/reagents ratios but failed for various resorcinarenes.[20,21] Under Gross−Rieche conditions ($SnCl_4$, Cl_2CHOCH_3) mono- and diformylation products were obtained in low yield (highest yield for diformylated product was 13% using 65 equiv of a formylating agent).[20,22] The Duff reaction under classical conditions (HMTA, AcOH) did not give product **2** in our hands. In 2012, Mendoza and co-workers reported on the beneficial application of microwaves in the Duff formylation of calix[4]- and calix[5]arenes in TFA.[23] We applied this microwave method to resorcin[4]arene **1** and obtained tetrasubstituted

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product **2** in 42% yield (Table 1, entry 1). Optimization of the reaction conditions allowed for the substantial reduction the amount of TFA and HMTA (Table 1, entry 2). Additionally, we tested microwave-free conditions at the same temperature (reaction in a sealed pressure vial). The product was obtained in 44% yield (entry 5). This result indicates that the microwave heating is not mandatory for effective formylation. However, under normal pressure and reflux conditions, the yield of **2** was lower even for longer reaction times (entries 7 and 8). An important feature of the developed synthetic procedure for synthesis of **2** is a simple, precipitation-based isolation method that allows for easy scale-up and therefore is highly beneficial for future applications of **2** as a building block.

Table 1. Synthesis of 2 (Scheme 1)

entry	C(**1**) (mM)	C(HMTA) (mM)	temp (°C)	time (h)	yield (%)
1	0.03	1.14	120 (MW)[a]	1	42
2	0.16	1.14	120 (MW)[a]	1	48
3	0.15	1.14	100 (MW)[a]	1	21
4	0.16	1.14	150 (MW)[a]	1	23
5	0.16	1.14	120[a]	1	44
6	0.16	1.14	120[a]	24	38
7	0.16	1.14	72	1	2
8	0.16	1.14	72	24	34

[a]Reaction in a sealed pressure vial, MW = microwave conditions.

The ^{1}H NMR spectrum of **2** in $CDCl_3$ reflects the C_4 symmetry of the molecule. The signal for a formyl group is observed at 10.3 ppm, and two separate OH signals appear at 8.4 and 13.1 ppm (at rt, Supporting Information). Such a large difference between OH groups indicates a system of two different intramolecular hydrogen bonds.[24,25] We assume that the low-field signal (13.1 ppm) comes from an OH group involved in hydrogen bonding with a carbonyl oxygen atom (stronger acceptor, better geometry), while the higher field signal (8.4 ppm) is for an OH group engaged in hydrogen bonding between neighboring phenolic rings. Interestingly, strong hydrogen bonding also leads to separation of signals for the aromatic carbon (six signals are present; see the Supporting Information). In a more polar solvent (DMSO-d_6), only one signal for the OH groups and four signals for the aromatic carbon atoms are present, indicative of fast exchange between the two forms (Supporting Information). The IR spectrum of **2** shows an intense absorption at 1639 cm^{-1}, characteristic of an aldehyde (Supporting Information).

Reaction of **2** with primary amines may lead to a variety of products due to the large number of possible regioisomers (or even atropoisomers) and also due to possible keto-enamine and enol-imine tautomers. On the basis of literature examples, it is not straightforward to predict the enol-imine versus keto-enamine equilibrium for resorcin[4]arene. Simple monosubstituted *N*-salicylideneanilines exist predominately in enol-imine forms.[26,27] Stable keto-enamine forms are observed for triimines of 2,4,6-triformylphloroglucinol (mixtures of regioisomers)[28] and diimines of 3,6-diformylcatechol.[29] However, to the best of our knowledge there are no examples of monoimines of 2-formylresorcinol. For previously reported mono- and diformylresorcin[4]arenes the conclusions were equivocal.[20]

We tested the reactivity of **2** toward various amines including aliphatic primary, secondary, and aromatic amines. For primary amines (both aliphatic and aromatic), the imine formation reactions proceeded smoothly without any catalyst in $CHCl_3$. All imine derivatives **3a–e** have simple NMR spectra (Figure 1). It indicates that the products exist in a highly symmetrical, single tautomeric forms. The number of ^{1}H and ^{13}C signals indicates that all arms are equivalent. In all cases, there are six different signals for carbon atoms of the resorcinol rings with one highly shifted toward low field (at approximately 168 ppm). The 2D COSY spectrum of **3a** detected coupling between NH protons and f as well as g protons (Figure 2a).

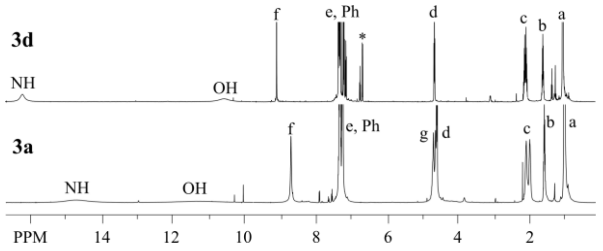

Figure 1. ^{1}H NMR spectra of **3a** and **3d** ($CDCl_3$, 600 MHz), The asterisk denotes residual aniline; for atom numbering, see Scheme 1; g, NCH_2Ph protons.

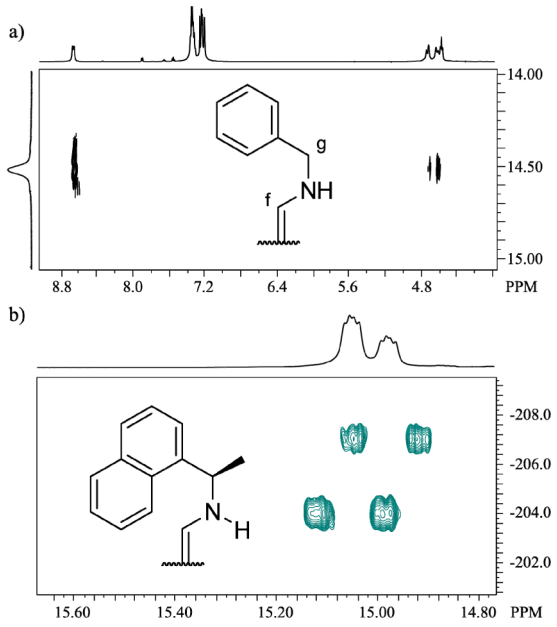

Figure 2. (a) Fragment of the ^{1}H–^{1}H COSY spectrum of **3a** (−25 °C) revealing the coupling between the NH proton and g and f protons; (b) ^{1}H–^{15}N HSQC spectrum of **3e** (−45 °C).

The spectra suggest exclusive (within the NMR detection limit) formation of keto-enamine tautomers. Additionally, the existence of **3a–e** in keto-enamine forms was confirmed using ^{1}H–^{15}N g-HMBC and HSQC experiments. In the spectra, the ^{15}N signals were observed at −204.6 and −201.8 ppm for **3b** and −184.2 ppm for **3d**. The nitrogen signals for **3e** were observed at −206.8 and −203.7 ppm. For enol-imines, ^{15}N signals are typically observed at −60 to −90 ppm.[30] For keto-enamines, ^{15}N signals are shifted and usually observed at −150 to −200 ppm.[31] The ^{1}H–^{15}N HSQC spectra of **3b** and **3e** confirmed that the proton resides at the nitrogen atom (with

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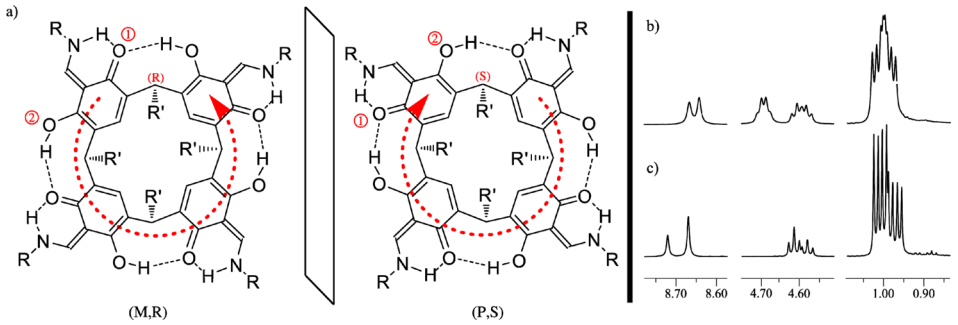

Figure 3. Inherently chiral forms of the keto-enamine tautomers of **3a–e** (a) (R groups according to Scheme 1, R′ denotes isobutyl). Fragments of ^{1}H NMR spectra of **3b** (b) and **3e** (c) showing the ratio of diastereoisomers ($CDCl_3$, 600 MHz).

a typical coupling constants for a single bond of 70 Hz, Figure 2b).

The number of signals in the NMR spectra suggest that keto-enamines **3a–e** have C_4 symmetry, indicating that all double bonds are formed highly regioselectively (Figure 3). The stabilization of this high-symmetry structure comes from the system of eight intramolecular hydrogen bonds (Figure 3). Indeed, in the solution both labile protons are highly shifted toward lower field (ca. 15 ppm and 13 ppm for NH and OH, respectively). The X-ray structure of **3a** also confirms the highly regioselective formation of the C_4 symmetric keto-enamine form (Figure 4 and Figure S34, Supporting Information). The

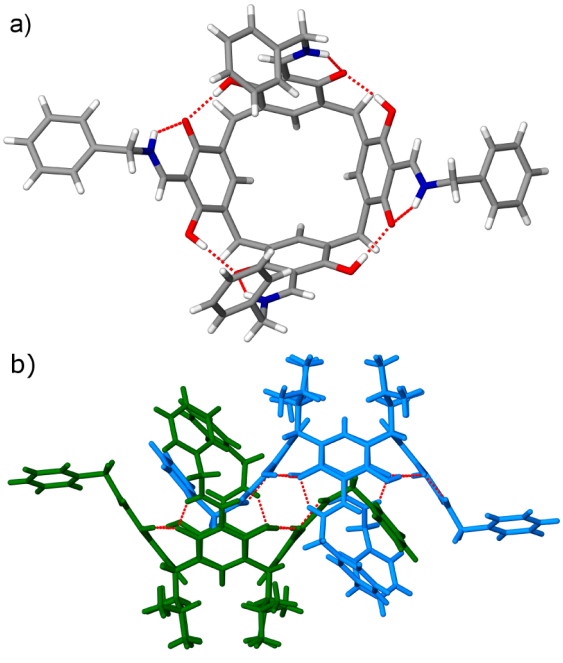

Figure 4. X-ray structure of keto-enamine **3a**: (a) top view (lower rim alkyl chains and solvent molecules were removed for clarity); (b) formation of a noncovalent dimer in the crystal lattice.

structure shows a systematic variation of bond lengths involving the whole keto-enamine fragment (Figure S35, Supporting Information). For example, all of the postulated C=O double bonds were found in the range of 1.298–1.310 Å, while all the postulated C–OH bonds were found in the range of 1.354–1.358 Å. Additionally, the system of hydrogen bonds (based on distances between non-hydrogen atoms) is also in agreement with the suggested structure.

The C_4 symmetry of a keto-enamine form implies that the whole molecule is propeller-shaped. This feature for cavity-containing molecules is known as inherent chirality.[25] Even without any additional stereogenic centers the molecule is chiral (although racemic for achiral amines). An additional stereogenic center, for example, coming from the amine part, should cause formation of diastereoisomers that can be detected using NMR. In order to prove this, we used chiral (*R*)-1-phenylethylamine. In the ^{1}H and ^{13}C NMR spectra we observed a double set of signals as compared with achiral analogues. All signals were assigned using 2D NMR spectra and are consistent with formation of two diastereoisomers of **3b** at 45:55 ratio. Using a more bulky amine, (*R*)-2-naphthylethylamine, diastereomeric induction is higher (dr 62:38 for **3e**). The 2D ROESY spectrum of **3b** showed no correlation between the two sets of signals. It confirmed that the signals do not come from a single less-symmetrical form (e.g., C_2 symmetrical). In order to find the possible chemical exchange between two diastereoisomers, EXSY experiments were performed using long mixing times (upper limit for EXSY experiments is set by relaxation time T1, in this case T1 = 1.4 s). No exchange was detected in this experiment. This result indicates that the diastereomeric C_4 symmetrical structures do not undergo exchange on the NMR time scale, meaning that the configuration of keto-enamines is quite stable. However, all attempts to separate diastereoisomers by chromatographic methods have been unsuccessful thus far.

A unique property of a dynamical system is the ability of self-sorting. This property allows for selective formation of thermodynamically favored structures even from complex mixtures of reagents. We have tested the chiral self-sorting abilities by application of racemic mixtures of chiral amines. For (*R,S*)-1-phenylethylamine the resulting mixture consisted of randomly substituted keto-enamines. However, for (*R,S*)-2-naphthylethylamine, the resulting mixture was identical to the one obtained for a single enantiomer (both ^{1}H and ^{13}C NMR, see the Supporting Information). These results indicate that the system is capable of very efficient self-sorting. Homochiral structures of C_4 symmetry are thermodynamically preferred. The plausible explanation of such preferences involves combination of three elements: (a) unidirectional system of hydrogen bonds; (b) regioselectivity of a keto-enamine form; and (c) bulky naphthyl substituents that can be conveniently arranged only in a propeller-like manner.

Application of secondary amines (e.g., diethylamine) in the reaction with **2** led to complicated mixtures of products. Although the enamine form is the only possible form for secondary amines, the products lack stabilization via hydrogen

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bonding. Additionally, test experiments with 2-formyl-4,6-di-*tert*-butylresorcinol[32] led to the formation of a mixture of decomposition products. These experiments indicate that stabilization by a system of hydrogen bonds is indispensable for tautomeric equilibrium and regioselectivity of the imine forming reaction.

In conclusion, we have applied a very simple, chromatography-free procedure for formylation of resorcin[4]arene **1**. This new building block is effective in regioselective formation of highly symmetrical imines. The imines of *O*-unprotected resorcin[4]arene exist in keto-enamine forms. These features have led to the formation of a new type of inherently chiral cavity-containing compounds due to regioselective unidirectional tautomerization. We predict that the resulting keto-enamine resorcin[4]arenes have greatly expanded cavities as compared to the parent resorcin[4]arenes due to coplanar arrangement of keto-enamine fragments. They also have modulated electronic properties as a result of the phenol rings existing in keto forms. Additionally, we have shown that the unidirectional pattern of keto-enamine groups have a great potential to drive the homochiral self-sorting. This ability opens up new possibilities into the construction of chiral cavitands and capsules in a dynamical way.

EXPERIMENTAL SECTION

Tetraformylresorcin[4]arene (2). Resorcin[4]arene (**1**) (0.606 g, 0.8 mmol) and urotropine (0.8 g, 5.7 mmol) were put in a 10 mL pressure vial. TFA (5 mL) was added, and the vial was shaken vigorously until the substrates were dispersed in the liquid. The vial was then put in a microwave reactor (CEM Discover SP with an infrared temperature sensor), heated to 120 °C with stirring for 1 h. The resulting dark solution was poured into a flask containing chloroform (25 mL) and aqueous HCl (25 mL, 1 M). The mixture was stirred vigorously overnight. The organic phase was separated, and the aqueous phase was washed with $CHCl_3$ several times (100 mL totally). The combined chloroform extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness. The resulting crude precipitate was washed with acetone (50 mL), filtered off, and vacuum-dried to afford 0.315 g of the yellow product (48%). Mp: 267 °C dec. ^{1}H NMR (DMSO-d_6/400 MHz): δ 10.89 (bs, 8H), 10.13 (s, 4H), 7.28 (s, 4H), 4.68 (t, 4H), 1.79 (t, 8H), 1.37 (m, 4H), 0.89 (d, 24H). ^{1}H NMR ($CDCl_3$/500 MHz): δ 13.14 (bs, 4H), 10.30 (bs, 4H), 8.35 (bs, 4H), 7.38 (bs, 4H), 4.48 (bt, 4H), 2.05 (bq, 8H), 1.46 (bm, 4H), 1.01 (bd, 24H). ^{13}C NMR (DMSO-d_6/100 MHz): δ 196.0, 157.4, 135.9, 123.5, 111.3, 44.1, 31.3, 26.3, 23.4. ^{13}C NMR ($CDCl_3$/125 MHz): δ 207.0, 195.8, 156.4, 155. 9, 131.8, 123.6, 123.1, 110.6, 41.8, 30.9, 29.4, 26.1, 22.7. Anal. Calcd for $C_{48}H_{56}O_{12}\cdot(CHCl_3)_n$ (chloroform also found in NMR spectra) (n = 1.17): C, 61.07; H, 5.50; Cl, 12.28. Found: C, 61.31; H, 5.99; Cl, 12.75. HRMS (ESI-TOF): calcd m/z for $C_{48}H_{56}O_{12}Na^+$ $[M + Na]^+$ 847.3669, found 847.3652.

Formation of Imines 3a–e: General Procedure. Tetraformylresorcinarene **2** (0.05 mmol, 41 mg) was put in a 2 mL pressure tube along with chloroform (2 mL). Amine (0.2 mmol) was then added with a syringe, the tube was sealed, and the solution was stirred. In a matter of minutes after the addition of the amine, the solution turned red and homogeneous. The solution was stirred overnight and evaporated to dryness. The resulting precipitate was vacuum-dried to afford the product (95–98% yield).

*Imine (**3a**).* ^{1}H NMR ($CDCl_3$/400 MHz): δ 14.84 (bs, 4H), 11.57 (bs, 4H), 8.68 (s, 4H), 7.40–7.20 (bm, 24H), 4.66 (bdd, 8H), 4.58 (bt, 4H), 2.08 (bm, 4H), 1.96 (bm, 4H), 1.56 (bm, 4H), 0.99 (bt, 24H). ^{13}C NMR ($CDCl_3$/100 MHz): δ 170.9, 163.0, 155.0, 136.1, 131.7, 129.2, 128.6, 128.4, 127.8, 117.7, 105.5, 56.2, 41.2, 30.7, 26.4, 23.5, 23.0. HRMS (ESI-TOF): calcd m/z for $C_{76}H_{85}N_4O_8^+$ $[M + H]^+$ 1181.6367, found 1181.6375.

*Imine (**3b**).* ^{1}H NMR ($CDCl_3$/600 MHz), mixture of diastereoisomers (most signals overlapping): δ 15.15 (bs, 8H), 11.53 (bs, 4H), 11.40 (bs, 4H), 8.67 (bs, 4H), 8.64 (bs, 4H), 7.40–7.15 (bm, 48H), 4.69 (bq, 8H), 4.59 (bm, 8H), 2.08 (bm, 8H), 1.96 (bm, 8H), 1.66 (bd, 24H), 1.57 (bm, 16H), 1.00 (bm, 48H). ^{13}C NMR ($CDCl_3$/100 MHz), mixture of diastereoisomers: δ 170.5, 170.0, 161.3, 161.2, 155.1, 154.9, 141.9, 141.7, 131.6, 131.3, 129.2, 129.1, 128.5, 128.3, 128.2, 127.9, 126.6, 126.3, 118.0, 117.9, 107.5, 107.4, 61.8, 61.3, 41.2, 41.1, 30.71, 30.68, 26.45, 26.41, 23.6, 23.48, 23.46, 23.05, 23.02. HRMS (ESI-TOF): calcd m/z for $C_{80}H_{93}N_4O_8^+$ $[M + H]^+$ 1237.6993, found 1237.6998.

*Imine (**3c**).* ^{1}H NMR ($CDCl_3$/400 MHz): δ 14.34 (bs, 4H), 12.03 (bs, 4H), 8.51 (bs, 4H), 7.18 (bs, 4H), 4.59 (bt, 4H), 3.38 (bm, 8H), 2.06 (bm, 4H), 1.95 (bm, 4H), 1.56 (bm, 12H), 1.23 (bm, 48H), 0.99 (bt, 24H), 0.86 (bm, 12H). ^{13}C NMR ($CDCl_3$/100 MHz): δ 172.4, 162.4, 155.2, 131.8, 129.0, 117.1, 107.2, 51.7, 41.1, 32.0, 30.8, 30.5, 29.4, 29.3, 26.8, 26.4, 23.5, 23.1, 22.9, 14.3. HRMS (ESI-TOF): calcd m/z for $C_{80}H_{125}N_4O_8^+$ $[M + H]^+$ 1269.9497, found 1269.9517.

*Imine (**3d**).* ^{1}H NMR ($CDCl_3$/600 MHz): δ 16.28 (bs, 4H), 10.59 (bs, 4H), 9.11 (bs, 4H), 7.40–7.30 (20H), 7.21 (bt, 4H), 4.67 (t, 4H), 2.11 (m, 8H), 1.62 (m, 4H), 1.06 (bt, 24H). ^{13}C NMR ($CDCl_3$/150 MHz): δ 166.2, 157.2, 154.6, 142.6, 130.9, 129.6, 127.0, 126.9, 120.2, 119.6, 108.4, 41.3, 30.4, 26.2, 23.1, 22.8. HRMS (ESI-TOF): calcd m/z for $C_{72}H_{77}N_4O_8^+$ $[M + H]^+$ 1125.5741, found 1125.5747.

*Imine (**3e**).* ^{1}H NMR ($CDCl_3$/600 MHz), mixture of diastereoisomers: A δ 15.41 (bs, 4H), 11.41 (bs, 4H), 8.72 (bs, 4H), 7.99 (bd, 4H), 7.88 (bd, 4H), 7.80 (bd, 4H), 7.23 (bs, 1H), 5.52 (bq, 4H), 4.58 (bt, 4H), 2.06 (bm, 4H), 1.95 (bm, 4H), 1.80 (bd, 12H), 1.54 (bm, 4H), 0.97 (bdd, 24H); B δ 15.41 (bs, 4H), 11.59 (bs, 4H), 8.67 (bs, 4H), 7.92 (bd, 4H), 7.76 (bd, 4H), 7.40 (bt, 4H), 7.27 (bd, 4H), 7.21 (bs, 4H), 7.04 (bt, 4H), 5.45 (bq, 4H), 4.61 (bt, 4H), 2.08 (bm, 4H), 1.98 (bm, 4H), 1.75 (bd, 12H), 1.58 (bm, 4H), 1.01 (bdd, 24H). Overlapping aromatic signals in the range from 7.56 to 7.44 ppm. Their integration is consistent with four aromatic protons of A and two of B. The integration of the corresponding signals for A and B is in the ratio of A/B = 1: 1.4. ^{13}C NMR ($CDCl_3$/150 MHz), mixture of diastereoisomers: δ 170.3, 169.7, 161.2, 154.9, 154.7, 137.7, 137.2, 133.9, 133.8, 131.4, 131.1, 130.1, 129.8, 129.2, 129.0, 128.6, 128.2, 128.1, 126.7, 126.6, 125.83, 125.75, 125.63, 125.45, 123.7, 123.3, 122.4, 117.9, 117.7, 107.5, 107.4, 57.63, 57.58, 41.0, 40.9, 30.51, 30.46, 26.2, 23.22, 23.20., 23.19, 22.9, 22.82, 22.79. HRMS (ESI-TOF): calcd m/z for $C_{96}H_{101}N_4O_8^+$ $[M + H]^+$ 1437.7619, found 1437.7617.

Crystal data for 3a: $C_{95.50}H_{110}N_4O_9$ (**3a** × EtOH × $(toluene)_{2.5}$), M = 1457.88, orange prism, 0.35 × 0.21 × 0.14 mm^3, triclinic, space group P-1 (No. 2), a = 15.3492(3) Å, b = 15.6210(4) Å, c = 17.0234(2) Å, α = 89.136(2)°, β = 80.277(2)°, γ = 86.364(2)°, V = 4014.93(14) Å^3, Z = 2, D_c = 1.206 g/cm^3, F_{000} = 1566, Cu Kα radiation, λ = 1.5418 Å, T = 100.01(10) K, $2\theta_{max}$ = 143.2°, 63014 reflections collected, 15485 unique (R_{int} = 0.0608). Final GooF = 1.010, R1 = 0.0840, wR2 = 0.2447, R indices based on 13942 reflections with $I > 2\sigma(I)$ (refinement on F^2), 942 parameters, 26 restraints. Lp and absorption corrections applied, μ = 0.602 mm^{-1}. CCDC 965647 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

Supporting Information

NMR and MS spectra for enamines **3a–e**; ECD spectra for **3b** and **3e**; UV spectrum for **3b**; crystal structure for **3a**; NMR, MS, and IR spectra for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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