Self-association of branched and dendritic aromatic amides

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Several branched and dendritic aromatic amides have been obtained by reacting tris(4-aminophenyl)-methane 3 either with aryl iodide 1 in a Pd-catalysed carbonylation or with carboxylic acids in the presence of the coupling agent triphenyl phosphite. Nonpolar aromatic substituents and solubilising groups at the periphery ensured that the resulting oligoamides were soluble in chloroform, whereas amide groups in the structural centre of the molecules accounted for strong self-association through hydrogen bonding in solution as evidenced by ^{1}H NMR and vapour-pressure osmometry data. An alternative approach towards branched aramides is also presented which was based on the self-assembly of 1,3,5-tris(4,5-dihydroimidazol-2-yl)benzene 12 and various (amido)carboxylic acids.

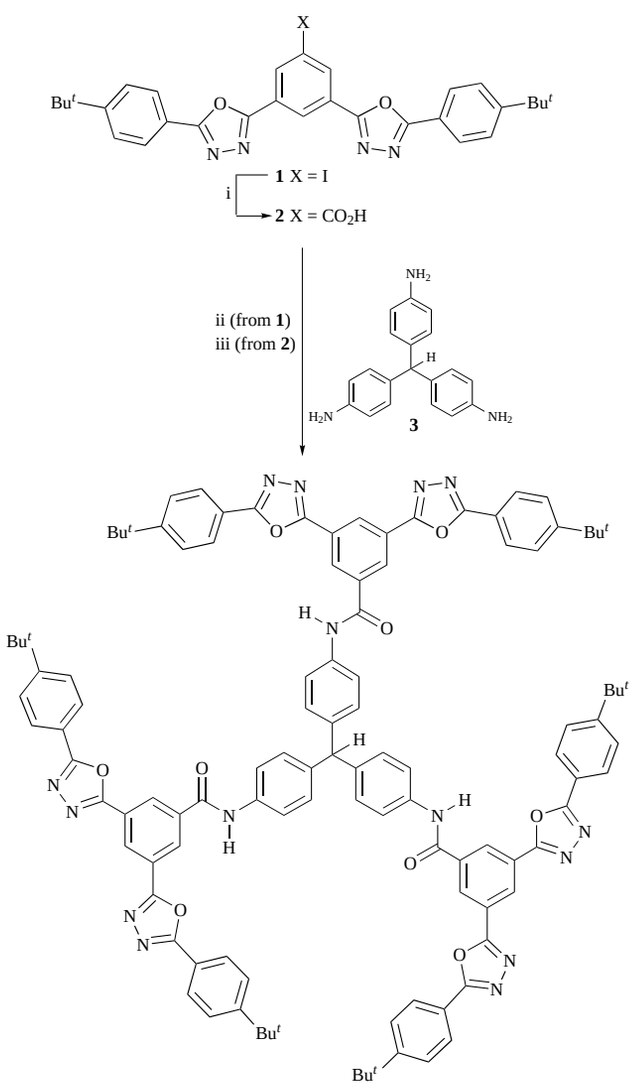
Introduction

Dendrimers with highly branched, spherical structures often possess unique properties such as unusually good solubility.[1] Linear poly(aramide)s are reputable high-performance fibre materials which owe their high tensile strength to a large degree of hydrogen bonding between aligned polymer chains; however, these polycondensates dissolve only in strong acids like concentrated sulfuric acid. The first poly(aramide) dendrimers were prepared several years ago by Feast[2] and Kim[3] and were found to be quite soluble in polar organic solvents (THF, DMSO, DMF). Whereas until about a year ago most reported dendrimer–dendrimer interactions were limited to micelle formation, aggregation or self-assembly in solution, or liquid-crystalline phase transitions in the absence of solvent,[4] the recent work by Zimmerman[5] and Meijer[6] has shown that non-covalent association processes can be useful for the preparation of large soluble structures. Our own interests in this area concentrated on chloroform-soluble dendrimers containing 1,3,4-oxadiazole systems and their strong tendency towards self-association.[7–8] Oxadiazoles are electron-deficient, 5-membered heterocycles and have shown promise as electron-transporting materials that enhance the efficiency of light-emitting diodes based on organic fluorescent dyes or conjugated polymers.[9] This report outlines how a combination of aramides and electron-deficient π-systems within a branched or dendritic structural entity leads to a class of highly chloroform-soluble compounds with solution properties dominated by hydrogen-bonding interactions between dissolved molecules.

Results and discussion

Synthesis and self-association of covalently bonded branched aramides

Our synthesis of branched aramides made heavy use of palladium-catalysed carbonylations because these reactions proceed in high yield and are even suitable for polycondensations.[10] All investigated target compounds contained a triphenylmethane core derived from tris(4-aminophenyl)methane **3** that is easily available from a commercial dye in one step.[11] The synthesis of aryl iodide **1**, which introduces the oxadiazole motif, has been described elsewhere.[12] Palladium(0)-catalysed coupling of **1**, **3** and carbon monoxide proceeded smoothly in *N*-methylpyrrolidone (NMP) at 100 °C and with excess 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base, and gave triamide **4** in a single step (Scheme 1). Although the yield of crude product from the 7-component reaction was fairly good,



Scheme 1 *Reagents and conditions:* i, $LiOH·H_2O$, $PdCl_2$, $Ph_2P(m\text{-}C_6H_4SO_3Na)$, NMP, CO, 100 °C, 2 d, then HCl, 79–95%; ii, $PdCl_2$, $Ph_2P(m\text{-}C_6H_4SO_3Na)$, DBU, NMP, CO, 100 °C, 1 d, 31%; iii, $P(OPh)_3$, pyridine, 100 °C, 12 h, 43%

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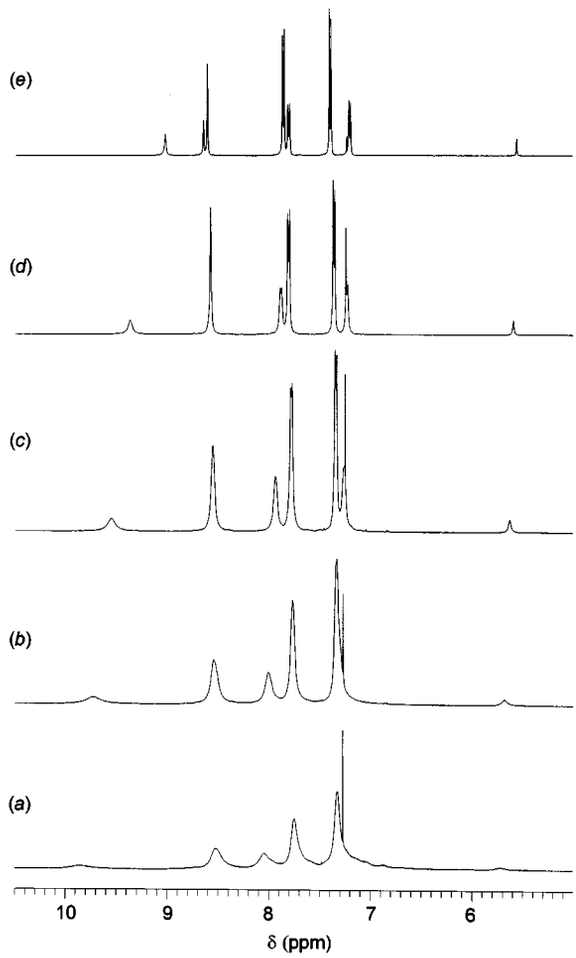
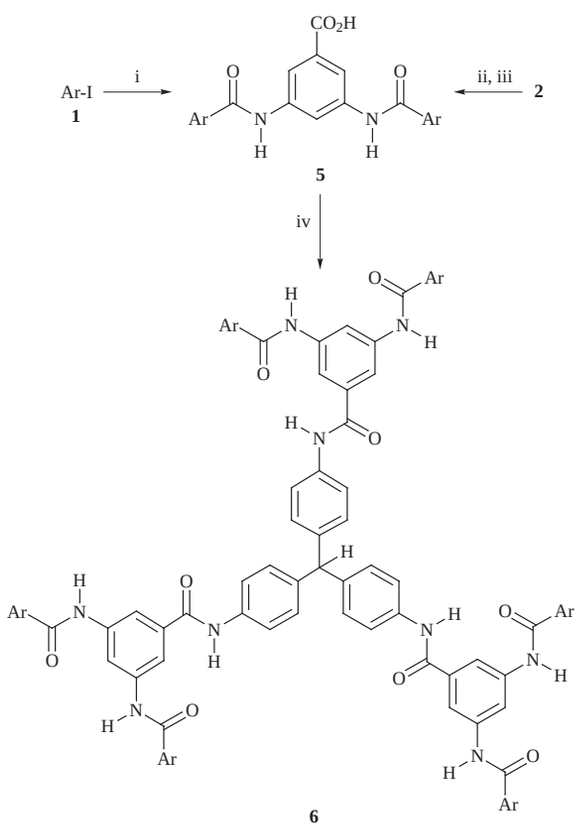


Fig. 1 ^{1}H NMR spectra (500 MHz, $CDCl_3$, 10^{-2} mol dm^{-3}, sealed tube) of **4** at various temperatures: (*a*) 20 °C; (*b*) 30 °C; (*c*) 40 °C; (*d*) 50 °C and (*e*) 70 °C, showing finally the sharp signals of nonassociated **4**

purification was hampered by a tendency of **4** to include impurities.‡ In particular, contamination of **4** by traces of the high-boiling solvent, NMP, used in the carbonylation reaction could not be overcome, and we finally decided to devise a different synthetic route that avoided altogether the need for NMP in the last step of the synthesis. Palladium-catalysed carbonylation of aryl iodide **1** in the presence of two equivalents of lithium hydroxide afforded carboxylic acid **2** in excellent yields. Subsequent condensation of the aromatic triamine **3** with acid **2** was conveniently achieved by applying triphenyl phosphite[13] in pyridine as condensing agent. The good solubility properties of **4** made it possible to omit an amidic cosolvent. Crude **4** obtained by this two step procedure was then readily purified by chromatography.

The nonpolar peripheral aromatic and the solubilising *tert*-butyl groups ensure that triamide **4** (formally a zeroth-generation 'dendrimer') is soluble in chloroform. On the other hand, the three amide groups in the centre of **4** are capable of hydrogen bonding. The compound strongly self-associates in solution as is apparent from a strong dependence of the ^{1}H NMR lineshapes of **4** on concentration, temperature and solvent, but not on spectrometer frequency. The NMR signals sharpen upon dilution below 10^{-3} mol dm^{-3}, addition of a polar cosolvent ([$^2H_6$]DMSO) or a raise in temperature above 70 °C (Fig. 1). Since the aromatic ^{1}H NMR signals ($\Delta\delta \leqslant \pm 0.2$) show only minor and the NH singlet ($\Delta\delta > 1$) considerable variations in chemical shift upon changes in concentration or temperature, hydrogen bonding is evidently the dominant intermolecular interaction whereas π–π interactions play, if at all, only a minor role. The concentration dependence of δ_{NH} allowed an association constant, K_a, of 790 ± 100 dm^3 mol^{-1} in dry $CDCl_3$ at 30 °C to be determined from ^{1}H NMR dilution experiments, assuming the isodesmic model of indefinite self-association.[14] Limited structural information is presently available for associated **4** which is believed to form predominantly disordered clusters in solution.[15] Vapour-pressure osmometry (VPO) studies in chloroform at 30 °C confirm that at comparatively low concentrations ($\geqslant$0.02 mol dm^{-3}) the number average molar mass M_n of **4** (see Experimental) is consistent with an average association degree of about 4 as would also be expected from its association constant.

The tendency towards self-association can be further enhanced by raising the number of amide groups per molecule as illustrated for nonaamide **6**, a first-generation dendrimer with regard to amide branches. Palladium-catalysed carbonylation of aryl iodide **1** in the presence of 3,5-diaminobenzoic acid afforded acid **5** (Scheme 2). Alternatively, monoacid **5** could



Scheme 2 *Reagents and conditions:* i, 3,5-diaminobenzoic acid, $PdCl_2$, $Ph_2P(m\text{-}C_6H_4SO_3Na)$, DBU, NMP, CO, 100 °C, 4 d, then HCl, 38%; ii, methyl 3,5-diaminobenzoate, $P(OPh)_3$, pyridine, 100 °C, 3 d, 68%; iii, NaOH, DMF, 120 °C, 4 d, then HCl, 58%; iv, **3**, $P(OPh)_3$, pyridine, 100 °C, 12 h, 37%

be obtained by the coupling of carboxylic acid **2** and methyl 3,5-diaminobenzoate with $P(OPh)_3$, followed by saponification of the methyl ester. Linking monoacid **5** and tris(aniline) **3** together was again accomplished with the amide coupling reagent $P(OPh)_3$.

The solubility of nonaamide **6** in chloroform exceeds 200 mg cm^{-3}, and is over four times larger than that of **4**. This was not entirely unexpected since (particularly higher-generation) dendrimers are known to be much more soluble than any of their related linear or slightly branched polycondensates and because the solution properties of dendrimers are mainly determined by

‡ For this reason, PPh_3 was replaced by a water-soluble sulfonated triphenylphosphine derivative, $Ph_2P(m\text{-}C_6H_4SO_3Na)$, as ligand for the Pd catalyst since the latter was easily removed during aqueous work-up.[18]

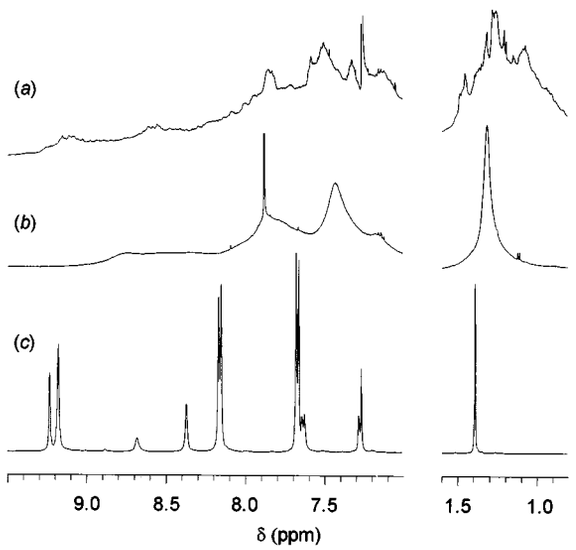
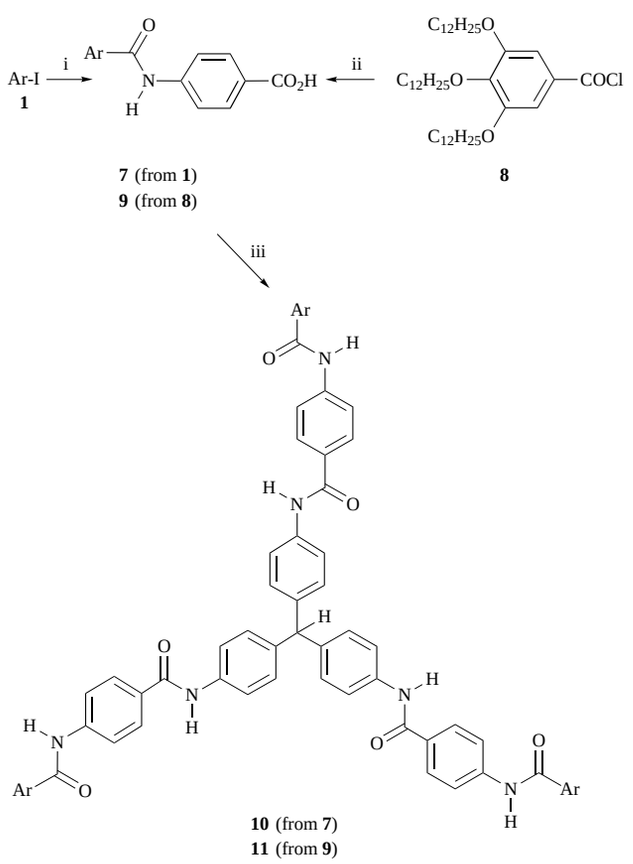


Fig. 2 ^{1}H NMR spectra (500 MHz, 25 °C) of **6** in various solvents: (*a*) $CDCl_3$; (*b*) $CDCl_3$–[$^2H_6$]DMSO, 6 : 1; (*c*) $CDCl_3$–CF_3CO_2D, 6 : 1

the polarity of the periphery.[1] Although nonaamide **6** has nonpolar substituents at its perimeter, the nine amide groups in the centre are accessible for intermolecular hydrogen bonding interactions and enhance the probability of multiple interactions. A much stronger association is evident from the broad and structureless ^{1}H NMR signals of the aromatic as well as *tert*-butyl protons of **6** in $CDCl_3$ at room temperature [Fig. 2(*a*)] and the spectrum does not simplify even upon heating up to 138 °C in [$^2H_2$]tetrachloroethane. Although addition of [$^2H_6$]DMSO causes some reduction in linewidth [Fig. 2(*b*)], a more polar cosolvent, such as trifluoroacetic acid, is necessary to break all inter-dendrimer hydrogen bonds [Fig. 2(*c*)].



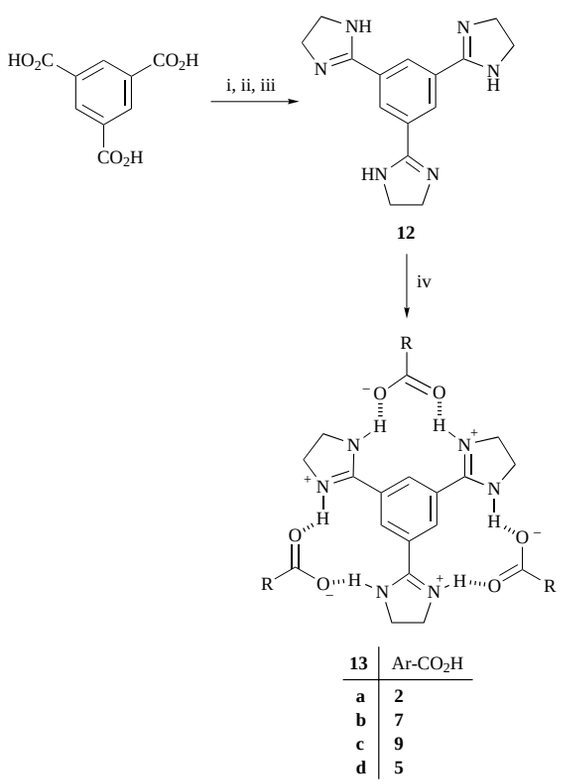
Scheme 3 *Reagents and conditions:* i, 4-aminobenzoic acid, $PdCl_2$, $Ph_2P(m\text{-}C_6H_4SO_3Na)$, DBU, NMP, CO, 100 °C, 2 d, then HCl, 28%; ii, 4-aminobenzoic acid, NMP, 47%; iii, **3**, $P(OPh)_3$, pyridine, 100 °C, 3 d, 15–68%

Furthermore, solubility in nonpolar solvents demands a sufficient degree of branching. We tested this assumption by preparing branched compounds **10** and **11** by similar amide coupling techniques as discussed before (Scheme 3). Both compounds have fewer amide groups than **6** but more than **4**. Whereas the higher degree of branching in **6** counteracts the solvophobic effect of the extra amide groups, **10** with its linear aramide arrangement no longer dissolves in chloroform without the addition of a cosolvent (*e.g.* [$^2H_6$]DMSO).

Aromatic substituents have also a considerable influence on association. The 3,4,5-tris(dodecyloxy)phenyl-substituted derivative **11** dissolves easily in $CDCl_3$ as a result of its long alkoxy solubilising groups. Its association constant K_a of 570 ± 200 dm^3 mol^{-1} in chloroform at 25 °C is comparable to that of **4** despite the doubled number of amide groups. It has been noted by Sanders and Hunter that strong aromatic–aromatic interactions occur not only between donor- and acceptor-substituted arenes but also between electron-deficient π-systems.[16] This correlates with our observation that incorporation of electron-deficient oxadiazole groups increases association in comparison to a compound such as **11** which has electron-rich aromatic substituents and lacks the synergy between attractive π-interactions and hydrogen bonding.

Hydrogen-bonded assemblies containing aramides

We wondered whether or not hydrogen bonding could also be applied for constructing branched aramide structures by self-assembly. This approach would have the particular advantage of requiring smaller building blocks (for practical purposes we chose acid derivatives, *e.g.* **2**, **7** or **9**) that are easier to synthesise and to purify than a comparably large covalently-bonded branched compound or dendrimer. One of us has recently found that the tris(imidazoline) base **12** (prepared in one step from 1,3,5-benzenetricarboxylic acid and 1,2-ethylenediamine in ethylene glycol) forms hydrogen-bonded salts **13** with three equivalents of a carboxylic acid (Scheme 4).[17] If the acid component contains suitable



13	Ar-CO_2H
a	**2**
b	**7**
c	**9**
d	**5**

Scheme 4 *Reagents and conditions:* i, $H_2NCH_2CH_2NH_2$, H_2NCH_2-CH_2NH_2·2 HCl, *p*-TsOH, ethylene glycol, reflux, 3 h; ii, HCl; iii, NaOH, 31–64%; iv, $ArCO_2H$ (3 equiv.), EtOH–$CHCl_3$, reflux, 61–87%

solubilising groups, the resulting noncovalent complexes **13** become soluble in chlorinated and aromatic solvents. Such complexes have dissociation constants of $\leqslant 10^{-4}$ mol dm^{-3} in chloroform at 25 °C and the η^2-bridged arrangement of the carboxylates in nonpolar solvents gives rise to a diagnostic ^{1}H NMR signal at $\delta \approx 10.1$ for the aromatic protons of the tris(imidazoline) core.

The formation of complexes **13** required simply dissolution of carboxylic acids **2**, **7**, **9** or **5** and tris(imidazoline) **12** in hot chloroform–ethanol. Crystallisation from solution took place upon partial evaporation of $CHCl_3$. The *as*-crystallised complexes **13a**–**c** redissolved without difficulty in neat chloroform (**13a**,**b**: 50–60 mg cm^{-3}; **13c**: >200 mg cm^{-3}); only the solubility of **13d** dropped to <10 mg cm^{-3}. Whereas **13a** showed sharp ^{1}H NMR signals in $CDCl_3$ even at high concentrations and gave no indication of self-association,[17] **13b** displayed broad and upfield-shifted NMR signals ($\Delta\delta \approx 0.5$) at concentrations $>2 \times 10^{-4}$ mol dm^{-3}, indicating strong association and some contribution by π-stacking. In contrast, the ^{1}H NMR spectra of **13c** showed little line-broadening but some self-association was evident from a small concentration dependence of the NH singlet's chemical shift from which a K_a of 40 ± 8 dm^3 mol^{-1} in $CDCl_3$ at 25 °C could be determined. A stronger self-association of **13b** compared to **13c** was also manifest from a steep rise in molar mass. Vapour-pressure osmometry measurements indicated an association degree of 3–4 for **13b** and ⩽1.3 for **13c**. This was yet another example where electron-deficient (hetero)aromatic substituents intensified the association behaviour. The NMR lineshapes of **13d**, on the other hand, could not be resolved even upon dilution to 10^{-4} mol dm^{-3}. Furthermore, strong aggregation finally limited the solubility in this case.

Conclusions

Although dendritic or star-branched poly(aramide)s may have comparatively low molar masses at a first glance, self-association in solution to large, albeit not well-defined, clusters makes these compounds behave like polymers with increased viscosity and effective molar mass even in dilute solutions. Whereas polymers suffer from a lack of purification methods that makes it difficult to remedy any incorporated structural defects, dendrimers and related branched compounds can be more easily purified. The concept of using (self-assembly and) self-association for the preparation of large, higher-molar-mass clusters in solution is, however, a 'tightrope walk' since insoluble aggregates and gels have to be avoided. If the associating compound contains solubilising groups and a branched structure, high solubility and self-association no longer exclude each other. Possible applications for such self-associating, branched poly(aramide)s with peripheral electroactive groups will be reported in due course.

Experimental

General

All solvents were distilled prior to use. Melting points: Olympus BH-2 polarisation microscope with Linkam TMS91 programmable sample heater. NMR: Varian VXR 300, Bruker DRX 500; TMS was used as internal standard for NMR measurements in nonaqueous solvents or sodium 3-(trimethylsilyl)-2,2,3,3-[^{2}H$_4$]propionate in D_2O; *J* values are given in Hz; the multiplicities of ^{13}C signals were determined by DEPT experiments. IR: Perkin-Elmer Ratio Recording Infrared Spectrophotometer 1420, Bruker Vector 22 FT-IR. Gel permeation chromatography (GPC): Waters 510 pump and Waters 410 differential refractometer; columns: Polymer Standards SCV 10^3 Å and 10^4 Å; eluent: THF; flow: 1 cm^3 min^{-1}; calibration against polystyrene standards. MALDI-TOF-MS: self-constructed time-of-flight mass spectrometer (Organisch-chemisches Institut, University of Münster); matrix: 2,5-dihydroxybenzoic acid; ionisation: N_2 laser (337 nm, 3 ns pulses); acceleration voltage: 16 kV; flight path: 1 m; mass accuracy: ±0.1%. VPO: Knauer vapour pressure osmometer. TLC: Aluminium sheets with silica gel $60F_{254}$ (Merck). Chromatography: ICN silica gel 32–63 (ICN Biomedicals). Elemental analyses: Pharmaceutical Institute of the Heinrich Heine University, Düsseldorf. Compounds **1**,[12] **3**,[11] $Ph_2P(m\text{-}C_6H_4SO_3Na)$,[18] *N*,*N*′,*N*″,*N*‴-tetraethylisophthalamidine,[19] **8**[20] were prepared by literature procedures.

Triamide 4 (carbonylation route)

A solution of **1** (1.81 g, 3.00 mmol), **3** (289 mg, 1.00 mmol), $PdCl_2$ (31.8 mg, 0.18 mmol), $Ph_2P(m\text{-}C_6H_4SO_3Na)$ (216 mg, 0.54 mmol) and 1-methyl-2-pyrrolidinone (NMP) (12 cm^3) was stirred at 100 °C under N_2 for 15 min. The reaction flask was flushed with carbon monoxide (which was obtained from heating 8.0 g of sodium formate and 10 cm^3 of conc. H_2SO_4 to 120 °C, condensing the CO in a liquid-N_2 trap and allowing the gas to evaporate again), and connected with a CO-filled gas burette. After addition of DBU (0.43 cm^3, 3.6 mmol), the brown suspension was stirred at 100 °C for 5 h until the theoretical amount of CO (about 66 cm^3) had been consumed. The solvent was then removed by vacuum distillation (60 °C/0.04 mbar). The residual grey solid (1.85 g) was extracted with hot ethanol (90 cm^3), collected by suction filtration and dried. Purification by column chromatography ($CHCl_3$–MeOH, 35:1 to 15:1) and crystallisation, after slow evaporation of the eluent, and drying at 100 °C/10^{-4} mbar afforded **4** as a colourless solid (560 mg, 31%) that contained still about 2% of NMP.

3,5-Bis[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl]benzoic acid 2

A solution of **1** (4.81 g, 8.00 mmol), lithium hydroxide hydrate (672 mg, 16.0 mmol), $PdCl_2$ (54.8 mg, 0.244 mmol) and $Ph_2P(m\text{-}C_6H_4SO_3Na)$ (293 mg, 0.732 mmol) in NMP (20 cm^3) was stirred under N_2/CO at 100 °C for 24 h until consumption of carbon monoxide had ceased. The yellow–brown solution was added dropwise to water (100 cm^3)/conc. HCl (2 cm^3) under vigorous stirring. The brown precipitate was then collected by suction filtration, dried and purified by column chromatography (for this, a concentrated solution of the crude product in $CHCl_3$ was prepared by treating the crude product first with $[NBu_4]OH$ or by complexation with **12** or with *N*,*N*′,*N*″,*N*‴-tetraethylisophthalamidine; eluent: ethyl acetate, then CH_2Cl_2–MeOH, 4:1) to yield **2** as a colourless solid (3.28 g, 79%). For analytical data see ref. 12.

Triamide 4 (amide coupling route)

A solution of **2** (1.50 g, 2.87 mmol), **3** (277 mg, 0.957 mmol) and $P(OPh)_3$ (0.90 cm^3, 3.4 mmol) in pyridine (20 cm^3) was heated to 90 °C for 12 h. About half of the solvent was then removed by distillation and the remaining red–brown solution was added dropwise to ethanol (100 cm^3). A rose-coloured precipitate (1.45 g) was collected by suction filtration and dried. Purification of the crude product by column chromatography (CH_2Cl_2–MeOH, 25:1) afforded **4** as a colourless solid (740 mg, 43%), mp 270–285 °C [Found: C, 74.4; H, 5.8; N, 11.6. $C_{112}H_{103}N_{15}O_9$ (1803.16) requires C, 74.6; H, 5.8; N, 11.7%]; $\lambda_{max}(CH_2Cl_2)$/nm 295 (ε/dm^3 mol^{-1} cm^{-1} 19 600); ν_{max}(KBr)/cm^{-1} 2963, 1676, 1614, 1512, 1495, 1413, 1253, 843, 720; δ_H(500 MHz, $CDCl_3$–CF_3CO_2D, 3:5) 1.45 (s, CH_3), 5.80 (s, Ar_3CH), 7.35 and 7.77 [AA′XX′, $(C_6H_4)_3C$], 7.79 and 8.24 (AA′XX′, Bu^{t}C$_6$H$_4$), 9.27 (3 H, t, *J* 1.6) and 9.29 (6 H, d, *J* 1.6, C_6H_3); δ_C(75 MHz, $CDCl_3$–[$^2H_6$]DMSO, 6:1) 31.05 (CH_3), 35.05 [$C(CH_3)_3$], 55.47 (weak signal, Ar_3CH), 120.94, 126.06, 126.53, 126.81, 128.65, 129.76 (arom. CH), 120.32, 125.00, 137.03, 137.38, 140.18, 155.68, 162.59, 164.13, 165.03 (*ipso*-C, C=O, C=N); *m*/*z* (MALDI-TOF) 1826 (80%, M + Na$^+$), 1804 (100,

M + H$^+$); M_n (VPO, $CHCl_3$, 35 °C, 21–49 mg g^{-1}) 7330 g mol^{-1} (against benzil as standard), 7120 g mol^{-1} (against polystyrene 2000 as standard), 7530 g mol^{-1} (against polystyrene 5000 as standard); R_f(CH_2Cl_2–MeOH, 20:1) 0.23.

3,5-Bis{3,5-bis[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl]-benzoylamino}benzoic acid 5

Carbonylation route. The synthesis was carried out as described for **4** with **1** (5.12 g, 8.00 mmol), 3,5-diaminobenzoic acid (609 mg, 4.00 mmol), $PdCl_2$ (85.3 mg, 0.481 mmol), $Ph_2P(m\text{-}C_6H_4SO_3Na)$ (578 mg, 1.44 mmol), DBU (2.2 cm^3, 14.4 mmol) and NMP (20 cm^3). Purification by chromatography ($CHCl_3$–MeOH, 9:1) and recrystallisation from hot $CHCl_3$ (60 cm^3)–EtOH (40 cm^3) gave a colourless solid (1.78 g, 38%), mp 285–287 °C [Found: C, 71.1; H, 5.7; N, 12.0. $C_{69}H_{64}N_{10}O_8$ (1161.33) requires C, 71.4; H, 5.6; N, 12.1%]; ν_{max}(KBr)/cm^{-1} 2963, 1682, 1615, 1548, 1495, 1455, 1268, 842, 720; δ_H(300 MHz, $CDCl_3$–[$^2H_6$]DMSO, 6:1) 1.37 (s, CH_3), 7.57 and 8.08 (AA′XX′, Bu^tC_6H_4), 8.24 (2 H, d, *J* 1.6) and 8.94 [1 H, t, *J* 1.6, $(RNH)_2C_6H_3CO_2H$], 8.89 (2 H, t, *J* 1.5) and 9.00 [4 H, d, *J* 1.5, C_6H_3], 10.71 (s, NH); δ_C(75 MHz, $CDCl_3$–[$^2H_6$]DMSO, 6:1) 31.00 (CH_3), 35.00 [*C*(CH_3)$_3$], 117.24, 117.94, 126.05, 126.80, 128.86 (arom. CH, 1 signal not resolved), 120.45, 125.04, 131.58, 136.85, 139.12, 155.59, 162.83, 163.57, 165.03, 167.56 (*ipso*-C, C=N, C=O); *m*/*z* (MALDI-TOF) 2348 (M_2 + Na$^+$), 1186 (M + Na$^+$), 1163 (M + H$^+$); R_f(ethyl acetate) 0.01; R_f($CHCl_3$–MeOH, 9:1) 0.12.

Amide coupling route. A solution of methyl 3,5-diaminobenzoate (prepared in 96% yield from 3,5-diaminobenzoic acid, methanol and conc. HCl, and purified by sublimation at 320 °C/0.01 mbar) (665 mg, 4.00 mmol), **2** (4.18 g, 8.00 mmol) and $P(OPh)_3$ (2.7 cm^3, 9.6 mmol) in pyridine (50 cm^3) was stirred at 100 °C for 3 d. The colourless precipitate (3.20 g, 68%) that had formed during this period was collected by suction filtration and dried, mp 249–259 °C [Found: C, 71.2; H, 5.8; N, 11.6. $C_{70}H_{66}N_{10}O_8$ (1175.36) requires C, 71.5; H, 5.7; N, 11.9%]; ν_{max}(KBr)/cm^{-1} 2963, 1684, 1615, 1544, 1495, 1456, 1233, 1112, 1012, 720; δ_H(500 MHz, $CDCl_3$–CF_3CO_2D, 6:1) 1.38 (s, CH_3), 4.10 (s, OCH_3), 7.69, 8.18 (AA′XX′, Bu^tC_6H_4), 8.35 (2 H, br s), 8.86 [1 H, s, $(RCONH)_2C_6H_3CO_2CH_3$], 9.15 (4 H, br s), 9.23 (2 H, br s, C_6H_3CONH); *m*/*z* (MALDI-TOF) 1199 (25%, M + Na$^+$), 1177 (100, M + H$^+$); R_f(CH_2Cl_2–MeOH, 9:1) 0.70. A solution of the crude ester (2.43 g, 2.07 mmol) and NaOH (8.00 g, 200 mmol) in DMF (200 cm^3) was stirred at 120 °C for 4 d. A yellow precipitate formed and was collected by suction filtration. It was then partitioned between $CHCl_3$ (300 cm^3) and 2 M HCl (50 cm^3). The organic phase was separated, washed with 2 M HCl (50 cm^3) and water (50 cm^3), and concentrated in vacuum to afford **5** as a light yellow solid (1.39 g, 58%).

Dendrimer 6

Synthesis as described for **4** with **3** (55.4 mg, 0.191 mmol), **5** (662 mg, 0.574 mmol), $P(OPh)_3$ (0.18 cm^3, 0.69 mmol) and pyridine (1 cm^3). The rose-coloured crude product was suspended in methanol and centrifuged. Purification by column chromatography (CH_2Cl_2–MeOH, 60:1) furnished **6** as a colourless solid (260 mg, 37%), mp 309–320 °C [Found: C, 72.8; H, 5.7; N, 12.5. $C_{226}H_{205}N_{33}O_{21}$ (3719.35) requires C, 73.0; H, 5.6; N, 12.4%]; ν_{max}(KBr)/cm^{-1} 2963, 1670, 1614, 1542, 1495, 1447, 1413, 1268, 1253; δ_H(500 MHz, $CDCl_3$–CF_3CO_2D, 7:3, 10^{-3} mol dm^{-3}) 1.41 (s, CH_3), 5.76 (s, Ar_3CH), 7.30, 7.61 [AA′XX′, $(C_6H_4)_3C$], 7.72, 8.18 (AA′XX′, Bu^tC_6H_4), 8.38 (6 H, d, *J* 1.5), 8.72 [3 H, t, *J* 1.5, $(RCONH)_2C_6H_3CO$], 9.23 (12 H, d, *J* 1.6), 9.27 (6 H, t, *J* 1.6, C_6H_3CONH); δ_C(125 MHz, $CDCl_3$–CF_3CO_2D, 6:1) 31.47 (CH_3), 36.19 [*C*(CH_3)$_3$], 56.30 (weak signal, Ar_3CH), 118.89, 119.58, 123.73, 127.74, 128.59, 130.18, 131.08, 131.10 (arom. CH), 118.29, 125.48, 134.87, 136.20, 136.70, 138.76, 143.02, 159.85, 163.59, 165.79, 167.61, 169.09 (*ipso*-C, C=O); *m*/*z* (MALTI-TOF) 3741 (100%, M + Na$^+$), 3721 (75, M + H$^+$); M_n (GPC) 4570 (M_w/M_n = 1.06); M_n (VPO, $CHCl_3$, 35 °C, 15–41 mg g^{-1}) 16 500 g mol^{-1} (against benzil as standard), 16 000 g mol^{-1} (against polystyrene 2000 as standard), 17 000 g mol^{-1} (against polystyrene 5000 as standard); R_f(CH_2Cl_2–MeOH, 9:1) 0.5.

4-{3,5-Bis[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl]-benzoylamino}benzoic acid 7

Synthesis as described for **4** with **1** (6.41 g, 10.0 mmol), 4-aminobenzoic acid (1.37 g, 10.0 mmol), $PdCl_2$ (73.3 mg, 0.413 mmol), $Ph_2P(m\text{-}C_6H_4SO_3Na)$ (497 mg, 1.24 mmol), DBU (3.6 cm^3, 24.0 mmol) and NMP (30 cm^3) yielded **7** (1.80 g, 28%) as a colourless solid after purification by column chromatography (hexane–CH_2Cl_2–ethyl acetate, 4:1:1, followed by ethyl acetate, then $CHCl_3$–MeOH, 9:1 up to 4:1), mp 355 °C (Found: C, 69.3; H, 5.5; N, 10.4. $C_{38}H_{35}N_5O_5\cdot H_2O$ requires C, 69.2; H, 5.7; N, 10.6%); ν_{max}(KBr)/cm^{-1} 2963, 1689, 1600, 1531, 1495, 1409, 1252, 1176, 1112, 843, 720; δ_H(500 MHz, $CDCl_3$–[$^2H_6$]DMSO, 1:1) 1.40 (s, CH_3), 7.62 and 8.13 (AA′XX′, Bu^tC_6H_4), 7.99 and 8.03 (AA′BB′, $RCONHC_6H_4CO_2H$), 8.96 (1 H, t, *J* 1.6) and 8.99 (2 H, d, *J* 1.6, C_6H_3), 10.83 (s, NH); δ_C(75 MHz, $CDCl_3$–CD_3OD, 6:1) 31.16 (CH_3), 35.34 [*C*(CH_3)$_3$], 120.18, 126.51, 127.18, 127.49, 128.91, 131.17 (arom. CH), 120.26, 125.46, 126.56, 137.43, 142.74, 156.54, 163.09, 164.70, 165.82, 168.70 (*ipso*-C, C=N, C=O); *m*/*z* (CI, NH_3) 659 (100%, M + NH_4^+), 642 (78, M + H$^+$), 194 (89), 177 (82); R_f(ethyl acetate) 0.56; R_f($CHCl_3$–MeOH, 9:1) 0.23.

4-[3,4,5-Tris(dodecyloxy)benzoylamino]benzoic acid 9

A solution of **8** (8.40 g, 12.1 mmol) and 4-aminobenzoic acid (1.66 g, 12.1 mmol) in NMP (40 ml) was stirred at 20 °C for 24 h, then poured into water (100 cm^3)/conc. HCl (2 cm^3). The light yellow precipitate was collected by suction filtration and further purified by column chromatography (hexane–ethyl acetate, 2:1). Recrystallisation from hexane–MeOH yielded 4.53 g (47%) of a colourless solid, mp 183 °C [Found: C, 75.5; H, 10.4; N, 1.6. $C_{50}H_{83}NO_6$ (794.22) requires C, 75.6; H, 10.5; N, 1.8%]; ν_{max}(KBr)/cm^{-1} 2924, 2853, 1689, 1596, 1530, 1426, 1338, 1118; δ_H(300 MHz, $CDCl_3$, 0.125 mol dm^{-3}) 0.88 (9 H, ~t, *J* 6.4, CH_3), 1.20–1.38 (m, 24 H), 1.38–1.52 (m, 6 H), 1.70–1.83 (m, 6 H, CH_2), 3.96 (4 H, t, *J* 6.4, OCH_2), 4.01 (2 H, t, *J* 6.4, OCH_2), 7.02 (2 H, s, C_6H_2), 7.78 and 8.11 (AA′XX′, C_6H_4), 8.25 (1 H, s, NH); δ_C(75 MHz, $CDCl_3$) 14.14 (CH_3), 22.72, 26.09, 29.34, 29.40, 29.43, 29.46, 29.62, 29.69, 29.74, 29.78, 30.33, 31.95, 69.37, 73.60 (CH_2), 105.71, 119.28, 131.56 (arom. CH), 124.81, 129.32, 141.55, 143.06, 153.18, 166.09, 171.39 (*ipso*-C, C=O); *m*/*z* (EI, 70 eV) 796 (68%, M$^+$), 659 (40), 490 (74); R_f(hexane–ethyl acetate, 2:1) 0.16.

Hexaamide 10

Synthesis as described for **4** with **7** (642 mg, 1.00 mmol), **3** (95.5 mg, 0.333 mmol), $P(OPh)_3$ (0.32 cm^3, 1.2 mmol) and pyridine (5 cm^3). The crude product was purified by crystallisation from $CHCl_3$–MeOH and column chromatography (CH_2Cl_2–MeOH, 15:1) to give **10** as a colourless solid (110 mg, 15%), mp 297–300 °C [Found: C, 72.8; H, 5.3; N, 11.6. $C_{133}H_{118}N_{18}O_{12}$ (2160.53) requires C, 73.9; H, 5.5; N, 11.7%]; ν_{max}(KBr)/cm^{-1} 2962, 1665, 1612, 1511, 1410, 1314, 1250, 1111, 843, 749, 719; δ_H(300 MHz, $CDCl_3$–[$^2H_6$]DMSO, 5:1) 1.39 (s, CH_3), 5.51 (s, Ar_3CH), 7.14 and 7.79 [AA′XX′, $(C_6H_4)_3C$], 7.58 and 8.07 (AA′XX′, Bu^tC_6H_4), 8.02 (~s, $RCONHC_6H_4CO$), 8.86 (t, *J* 1.5), 8.93 (d, *J* 1.5, C_6H_3), 9.89 (s, NH), 10.75 (s, NH); δ_C(125 MHz, $CDCl_3$–[$^2H_6$]DMSO, 5:1) 30.97 (CH_3), 34.97 [*C*(CH_3)$_3$], 55.17 (weak signal, Ar_3CH), 120.22, 120.84, 126.02, 126.55, 126.75, 128.47, 128.61, 129.46 (arom. CH), 120.26, 124.92, 130.60, 136.75, 137.19, 139.61, 141.50, 155.62, 162.53, 163.74, 164.93, 165.76 (*ipso*-C, C=O); *m*/*z* (MALDI-TOF) 2184 (75%, M + Na$^+$), 2161 (75, M + H$^+$); R_f(CH_2Cl_2–MeOH, 15:1) 0.58.

Hexaamide 11

Synthesis as described for **4** with **9** (1.55 g, 1.95 mmol), **3** (188 mg, 0.650 mmol), $P(OPh)_3$ (0.56 cm^3, 2.1 mmol), pyridine (1.5 cm^3) and NMP (3 cm^3) afforded **11** (1.15 g, 68%), mp 295–303 °C [Found: C, 77.4; H, 10.0; N, 3.1. $C_{169}H_{262}N_6O_{15}$ (2617.99) requires C, 77.5; H, 10.1; N, 3.2%]; ν_{max}(KBr)/cm^{-1} 2924, 2853, 1651, 1593, 1512, 1496, 1333, 1116; δ_H(500 MHz, $CDCl_3$, 3×10^{-4} mol dm^{-3}, all signals slightly broadened) 0.85–0.90 (9 H, m, CH_3), 1.21–1.37 (27 H, m), 1.42–1.51 (18 H, m, CH_2), 1.75 (6 H, qui, *J* 7.6), 1.81 (12 H, qui, *J* 7.6), 4.00 (12 H, t, *J* 6.3, OCH_2), 4.02 (6 H, t, *J* 6.3, OCH_2), 5.53 (s, Ar_3CH), 7.05 (s, C_6H_2), 7.11 and 7.56 [AA′XX′, $(C_6H_4)_3C$], 7.70 and 7.83 (AA′BB′, $RCONHC_6H_4CO$), 8.03 (s, NH), 8.08 (s, NH); δ_C(75 MHz, $CDCl_3$–[$^2H_6$]DMSO, 6:1) 14.05 (CH_3), 22.49, 25.93, 25.99, 29.15, 29.22, 29.39, 29.43, 29.45, 29.50, 29.53, 29.56, 30.18, 31.71, 31.73 (CH_2), 56.32 (Ar_3CH), 68.95, 73.17 (OCH_2), 106.35, 119.76, 120.43, 128.42, 129.36 (arom. CH), 129.55, 129.97, 137.35, 139.38, 140.75, 142.16, 152.62, 165.54, 165.99 (*ipso*-C, C=O); *m*/*z* (MALDI-TOF) 2639 ($M + Na^+$); M_n (GPC) 4220 ($M_w/M_n = 1.03$); M_n (VPO, $CHCl_3$, 35 °C, 16–62 mg g^{-1}) 7190 g mol^{-1} (against benzil as standard), 6980 g mol^{-1} (against polystyrene 2000 as standard), 7380 g mol^{-1} (against polystyrene 5000 as standard); R_f(CH_2Cl_2–MeOH, 15:1) 0.84.

1,3,5-Tris(4,5-dihydro-1*H*-imidazol-2-yl)benzene 12

Benzene-1,3,5-tricarboxylic acid (1.51 g, 7.18 mmol), ethylenediamine (1.58 cm^3, 23.7 mmol), ethylenediamine dihydrochloride (3.15 g, 23.7 mmol), toluene-*p*-sulfonic acid (108 mg, 0.566 mmol) and ethylene glycol (10 cm^3) were heated to reflux for 3 h. About half of the ethylene glycol was then slowly removed by distillation. The residual solution was concentrated to dryness at reduced pressure (100 °C/0.02 mbar), and the residue was dissolved in water (40 cm^3)–conc. HCl (3 cm^3). Addition of 50% aqueous NaOH (3 cm^3) gave a yellow precipitate that was purified by another reprecipitation. Sublimation (325 °C/0.02 mbar) finally furnished yellow crystals (625 mg, 31%), mp 383–385 °C [Found: C, 64.0; H, 6.4; N, 29.7. $C_{15}H_{18}N_6$ (282.35) requires C, 63.8; H, 6.4; N, 29.8%]; ν_{max}(KBr)/cm^{-1} 3129, 2936, 2876, 1623, 1516, 1487, 1472, 1285, 1263, 981; *m*/*z* (CI, NH_3) 283, 282, 281 (53, 100, 83%, M^+), 254, 253, (58, 99), 240 (56), 224 (55); R_f(CH_2Cl_2–MeOH, 4:1) 0. The water-soluble hydrochloride **12**·3HCl was obtained as a light brown solid after freeze-drying a solution of **12** (225 mg, 0.797 mmol) in water (5 cm^3)/conc. HCl (10 drops), mp 339–340 °C (decomp.) [Found: C, 46.0; H, 5.6; N, 21.7. $C_{15}H_{21}N_6Cl_3$ requires C, 46.0; H, 5.4; N, 21.5%]; ν_{max}(KBr)/cm^{-1} 2923, 2853, 1647, 1601, 1582, 1380, 1335, 1116; δ_H(300 MHz, D_2O) 4.23 (s, CH_2), 8.58 (s, C_6H_3); δ_C(75 MHz, D_2O) 46.32 (CH_2), 126.52 (*ipso*-C), 133.93 (C_6H_3), 165.43 (C=N).

General procedure for the preparation of the complexes

Carboxylic acid (1.00 mmol) and **12** (0.333 mmol) were dissolved in hot ethanol (40 cm^3) to which a certain amount of $CHCl_3$ (5–40 cm^3) had been added as cosolvent. The solution was filtered whilst hot. After part of the chloroform was removed in vacuum, a fluffy, colourless precipitate separated upon cooling to room temperature.

Complex 13a. Yield: 87% [Found: C, 70.1; H, 6.1; N, 13.4; $C_{108}H_{108}N_{18}O_{12}$ (1850.17) requires C, 70.1; H, 5.9; N, 13.6%]; ν_{max}(KBr)/cm^{-1} 2963, 1635, 1616, 1581, 1495, 1392, 1366, 721; δ_H see ref. 17; δ_C(75 MHz, $CDCl_3$) 31.13 (CH_3), 35.16 [$C(CH_3)_3$], 45.66 (NCH_2), 126.15, 126.56, 126.94, 130.53, 134.95 (arom. CH), 120.77, 124.92, 125.49, 139.51, 155.68, 163.16, 163.54, 165.19, 170.93 (*ipso*-C, C=N, C=O).

Complex 13b. Yield: 70%, mp 245–248 °C [Found: C, 69.9; H, 5.8; N, 13.2. $C_{129}H_{123}N_{21}O_{15}$ (2207.52) requires C, 70.2; H, 5.6; N, 13.3%]; ν_{max}(KBr)/cm^{-1} 2962, 1666, 1603, 1525, 1494, 1377, 1251, 720; δ_H(500 MHz, $CDCl_3$–CD_3OD, 6:1) 1.39 (s, CH_3), 4.15 (s, NCH_2), 7.58 and 8.08 (AA′XX′, C_6H_4), 7.87 and 8.06 (AA′BB′, $NHC_6H_4CO_2^-$), 8.87 (6 H, br s) and 8.94 (3 H, br s, C_6H_3CONH), 9.45 (3 H, br s, C_6H_3); δ_C(75 MHz, $CDCl_3$–CD_3OD, 13:1) 31.07 (CH_3), 35.19 [$C(CH_3)_3$], 45.70 (NCH_2), 120.10, 126.30, 126.97, 127.28, 128.62, 130.39, 133.96 (arom. CH), 120.18, 125.15, 125.47, 132.66, 137.26, 140.77, 156.19, 162.76, 162.87, 164.36, 165.45, 173.25 (*ipso*-C, C=N, C=O); M_n (VPO, $CHCl_3$, 35 °C, 11–23 mg g^{-1}) 7620 g mol^{-1} (against benzil as standard), 8260 g mol^{-1} (against polystyrene 2000 as standard).

Complex 13c. Yield: 86%, mp 165–190/liquid crystal/237–238 °C/isotropic [Found: C, 74.2; H, 10.4; N, 4.4. $C_{165}H_{267}N_9O_{18}$ (2664.97) requires C, 74.4; H, 10.1; N, 4.7%]; ν_{max}(KBr)/cm^{-1} 2963, 1682, 1614, 1549, 1495, 1455, 1268, 1112, 843, 720; δ_H(300 MHz, $CDCl_3$, 10^{-2} M) 0.87 (27 H, ~t, *J* 6.4, CH_3), 1.19–1.38 (72 H, m), 1.38–1.52 (18 H, m), 1.70–1.85 (18 H, m, CH_2), 4.00 (18 H, m, OCH_2), 4.06 (12 H, br s, NCH_2), 7.10 (6 H, s, C_6H_2), 7.64 and 8.03 (AA′XX′, C_6H_4), 8.27 (3 H, s, NH), 9.87 (3 H, s, C_6H_3); δ_C(125 MHz, $CDCl_3$) 14.14 (CH_3), 22.73, 26.14, 26.17, 29.42, 29.44, 29.52, 29.67, 29.72, 29.75, 29.76, 29.81, 30.41, 31.96 (CH_2), 45.31 (NCH_2), 69.31, 73.54 (OCH_2), 105.86, 119.38, 130.33, 134.33 (arom. CH), 124.92, 129.53, 132.99, 140.50, 141.37, 153.18, 162.55, 165.71, 172.84 (*ipso*-C, C=O); M_n (VPO, $CHCl_3$, 35 °C, 27–54 mg g^{-1}) 3250 g mol^{-1} (against benzil as standard), 3510 g mol^{-1} (against polystyrene 2000 as standard).

Complex 13d. Yield: 61% [Found: C, 67.5; H, 5.6; N, 13.1. $C_{222}H_{210}N_{36}O_{24}$ (3766.33) requires C, 70.8; H, 5.6; N, 13.4%]; ν_{max}(KBr)/cm^{-1} 2962, 1680, 1615, 1550, 1494, 1268, 1112, 1101, 843, 786, 750, 720; δ_H(500 MHz, $CDCl_3$–CF_3CO_2D, 6:1) 1.41 (s, CH_3), 4.25 (s, NCH_2), 7.70 and 8.17 (AA′XX′, C_6H_4), 8.41 (6 H, d, *J* 1.9) and 8.88 [3 H, t, *J* 1.9, $(CONH)_2C_6H_3CO_2^-$], 8.76 (3 H, s, H, C_6H_3), 9.24 (18 H, m).

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