Phase Transfer Catalysis

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Pyridine-Bridged Benzimidazolium Salts: Synthesis, Aggregation, and Application as Phase-Transfer Catalysts**

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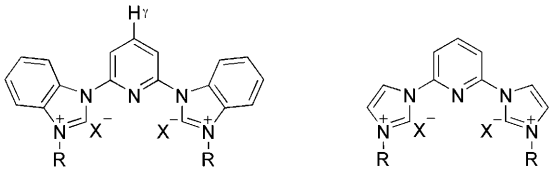
The benzimidazole skeleton is found in a variety of natural products.[1] Dimethylbenzimidazole, for example, is a key component in vitamin B_{12} and its derivatives. Besides its prominent role in pharmaceutical chemistry, the benzimidazole moiety also serves as a basis for ionic liquids[2] and as precursor for N-heterocyclic carbenes (NHCs).[3,4] Herein we show that benzimidazolium salts provide a novel structural motive for efficient, readily accessible, and easy-to-handle low-molecular-mass gelators (LMMGs) which are also suited as phase transfer catalysts (PTCs).

Owing to the physical properties of their gels, LMMGs and their potential applications have become a rapidly expanding interdisciplinary field of research. Hydrogen bonding, π-stacking, van der Waals, and dipole interactions are considered as the major physical and chemical interactions responsible for the formation of a three-dimensional network capable of the uptake and immobilization of solvents.[5,6] The majority of LMMGs that have been reported are based on cholesterol, amino acid, and carbohydrate skeletons having a multifunctional structure. A rational correlation of molecular structure and gelation ability in a given solvent still remains a challenge. Our interest in LMMGs derives from functional organometallics,[7] and we present benzimidazolium salts of type **1** (Scheme 1) as a simple structural motif.

The synthesis of bisbenzimidazolium salts **1** by reaction of 2,6-dibromopyridine[3] and N1-alkylated benzimidazoles[3] is troublesome and hampered by low yields, even under microwave conditions. In contrast, amination of 2,6-difluoropyridine with two equivalents of benzimidazole followed by N-alkylation with alkyl bromides or iodides in a sealed tube affords the bisbenzimidazolium salts **1a–e** in almost quantitative yields.[7a,8]



1a: R = *n*-$C_{16}H_{33}$; X = Br
1b: R = *n*-$C_{16}H_{33}$; X = I
1c: R = *n*-$C_{12}H_{25}$; X = I
1d: R = *n*-C_8H_{17}; X = I
1e: R = *n*-C_4H_9; X = I

2: R = *n*-$C_{16}H_{33}$; X = I

Scheme 1. Pyridine-bridged bisbenzimidazolium and bisimidazolium salts.

The gelation abilities of bisbenzimidazolium halides **1** were studied by heating them to reflux in a variety of protic and aprotic polar organic solvents, followed by cooling of the resulting solutions to room temperature. In general, bisbenzimidazolium salts **1a–d** form thermoreversible turbid gels within a few minutes in most polar solvents, such as acetic acid, acetonitrile, or various alcohols. For the shorter alkyl analogue **1e**, however, no gelation was observed under the same conditions. Gelation experiments with 2 wt% **1a–d** (wt/v; equal to 1.97×10^{-2} M for **1b**) in a selection of solvents are summarized in Table 1. Bisbenzimidazolium salts **1a–d** most efficiently gelate a wide structural variety of alcohols; firm gels were obtained from glycerol, 1,2-ethanediol, isopropanol, isobutanol, and also in acetonitrile. The gelation

Table 1: Gelation behavior of bisbenzimidazolium salts **1a–d** in selected solvents.[a]

Solvent	1a	1b	1c	1d	Solvent	1a	1b	1c	1d
Glycerol	G	G	G	G	*t*BuOH	WG	I[b]	I[b]	I
$(CH_2OH)_2$	G	G	G	G	MeCN	G	G	G	G
MeOH	C	G	S	S	AcOH	PG	G	G	WG
EtOH	PG	G	G	WG	Dioxane	G	G	PG	I
*n*PrOH	S	G	G	G	THF	P	G	PG	I
*i*PrOH	G	G	G	G	DCE	P	WG	PG	I
*n*BuOH	WG	G	G	G	Acetone	I	WG	WG	I
*i*BuOH	G	G	G	G	DMSO	P	PG	S	S

[a] Gelator concentration 2 wt%; C: crystal, G: gel, I: insoluble, PG: partial gel, P: precipitate, S: soluble, WG: weak gel. DCE = 1,2-dichloroethane. [b] At 1 wt% (upper limit of solubility), a weak gel is formed.

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ability decreases with the length of the alkyl chains. Whereas iodides **1c** and **1d** bearing C_{12} and C_8 alkyl groups are soluble in methanol, their C_{16} analogue **1b** induces gelation. This phenomenon, which is also observed with other polar solvents, such as acetic acid, dioxane, and THF, may suggest that van der Waals interactions between the alkyl chains of gelator and solvent molecules are crucial for the self-assembly process required for gelation. In contrast to iodide **1b**, the gelation ability of bromide **1a** in C_1–C_4 alcohols decreases with the alkyl chain length of the solvent used; from methanol, a needle-shaped crystal could even be grown. This observation indicates a significant influence of the counter-anion on the gelation.

The morphologies of selected typical three-dimensional networks of xerogels obtained from **1a–d** in *i*BuOH are presented in Figure 1. For **1a**, circa 250–500 nm wide and

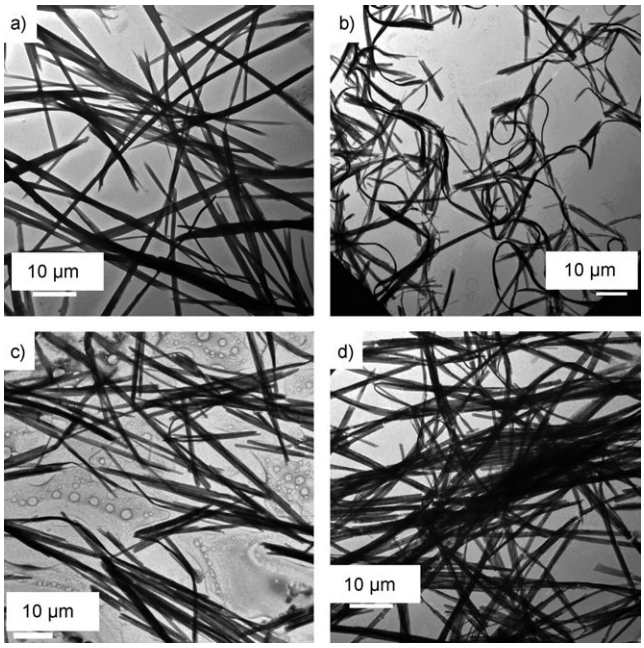


Figure 1. Selected transmission electron microscopy (TEM) images of gels formed with bisbenzimidazolium salts **1a–d** in *i*BuOH (3 wt%): Gel from a) **1a**, b) **1b**, c) **1c**, and d) **1d**.

several micrometer long straight fibers are observed (Figure 1a). Similar morphologies are also found in the gels **1c–d**/*i*BuOH (Figure 1c–d). Gel **1b**/*i*BuOH (Figure 1b) has twisted thin and long fibers (ca. 200 nm wide and several micrometers long) which are also observed in the gels obtained from **1b** with MeOH, EtOH, *n*PrOH, *i*PrOH, and *n*BuOH. Film-type morphologies are found in all the gels of **1a–d** formed with glycerol and 1,2-ethanediol.[8] Thinner and thicker straight fibers (ca. 200–400 nm wide and several micrometers long) are observed with gels **1a**/MeCN, **1b**/DCE and **1b**/THF.[8] A looser network consisting of thicker fibers (ca. 2 μm wide) is encountered in gels **1a**/EtOH, **1d**/EtOH, **1d**/MeCN, and gels **1a–d**/AcOH.[8] Morphologies of gels **1b**/acetone and **1b**/dioxane are similar, and have a densely structured film-type network.[8] A rod-like gel network consisting of fibers which are circa 200 nm wide and 1–2 μm long is observed in the partial gel **1b**/DMSO. All these morphologies indicate that the gels are formed by a parallel columnar packing self-assembly.

The gel–sol phase-transition temperatures (T_g) of gels in selected solvents were determined by the dropping ball method.[9] The stability of the gel network increases with the concentration and the length of the N-alkyl chain of the gelator, as established for the series **1b**/*n*BuOH, **1c**/*n*BuOH, and **1d**/*n*BuOH of gels, with concentrations varying from 0.5 to 5.0 wt% (Figure 2). At 3 wt%, T_g for gels **1d**/MeCN,

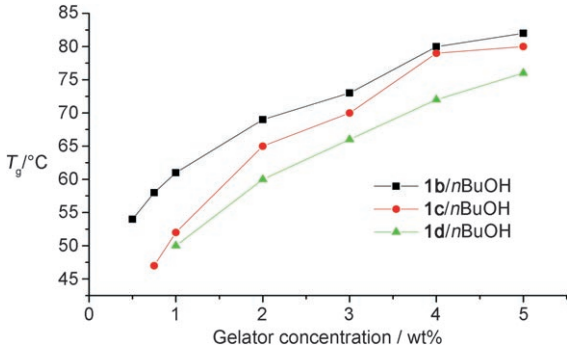


Figure 2. Correlation of gel–sol transition temperatures (T_g) for gels **1b–d**/*n*BuOH with gelator concentration.

1c/MeCN, **1a**/MeCN, and **1b**/MeCN increase in the order of 48 °C, 54 °C, 58 °C, and 78 °C; a similar trend was observed with gels **1a–d** with *i*BuOH, 1,2-ethanediol, and glycerol,[8] which further supports the superior aggregation potential of the counterion iodide in **1b** over bromide in **1a.**

Bisbenzimidazolium bromide **1a** is a rare example[10] of an efficient gelator which, despite having two long alkyl chains, could be characterized by single crystal X-ray crystallography (Figure 3). Analysis of a needle-type crystal grown from methanol reveals a network of a parallel array of columns (Figure 3d) which are held together by van der Waals interactions between the alkyl chains (H···H distances of 2.75–2.99 Å).[8] Hydrogen bonding and π stacking are the major interactions within these columns (fibers). Br···H distances of 2.6–3.4 Å indicate inter- and intramolecular hydrogen bonds between the molecules within the same layer.[8] Adjacent layers are connected by two different types of π stacking to form a unit: π–π interactions between both the pyridine rings (3.43 Å, Figure 3a) and between the phenyl rings of benzimidazole moieties (3.45 Å, Figure 3b) keep two layers together to form the structural unit of the column. These units are assembled by two strong hydrogen-bonding interactions (2.75 Å each, Figure 3c) between a bromide counterion and a hydrogen atom of the phenyl ring, and between another bromide ion and an NCH_2 hydrogen atom. These principal interactions, along with additional ionic interactions between the Br^- and N^+ centers, with the shortest distance being 3.55 Å (Figure 3a), may explain the efficient gelation ability of LMMGs **1.**

Shorter N-alkyl chains, such as in **1e**, suppress the ability to form gels. Instead, growth of single crystals having the

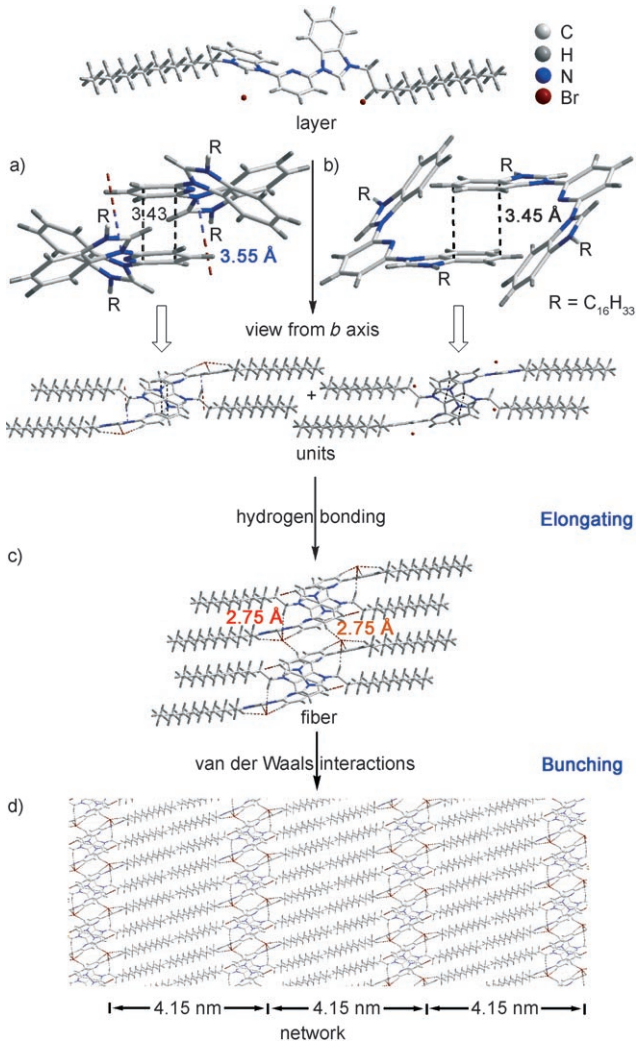


Figure 3. Structure of **1a** (crystal grown from methanol): a) π interaction between the pyridine rings from two adjacent layers, b) π interaction between phenyl groups of the two adjacent layers, c) hydrogen-bonding interactions connecting adjacent layers, d) part of the columnar structure of the truncated 2×2×2 array of unit cells (view along *b* axis).

composition **1e**·0.61 $CHCl_3$ and characterized by a similar parallel array of columns is favored.[8] The layers in the column are held together by π stacking (3.42 Å) between the phenyl rings, and by hydrogen bonding (2.99 Å). There are no obvious van der Waals interactions between the columns; instead, hydrogen bonds (3.12–3.15 Å) are responsible for the interactions of *n*-butyl groups with solvent guests.

The contribution of π stacking to the gelation process was evaluated by temperature-dependent ^{1}H NMR studies and by comparison of homologous bisbenzimidazolium (**1**) and bisimidazolium (**2**) salts.[7a] Broad NMR signals for the aromatic hydrogen atoms observed for gel **1b** (2 wt% in CD_3OD) at 298 K indicate extensive aggregation (Figure 4). Upon warming to 338 K by 10 K steps, the broad signals characteristic of the heteroaromatic protons and the NCH_2 atoms at 298 K steadily sharpen and are shifted downfield (e.g. the γ proton of the pyridine ring is shifted from 8.60 ppm

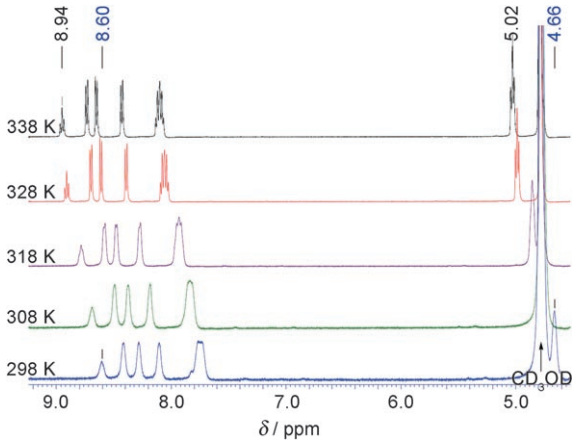


Figure 4. Temperature-dependent ^{1}H NMR spectra (aromatic and NCH_2 alkyl region) of a 2 wt% **1b**/CD_3OD gel.

to 8.94 ppm over a temperature range of 40 K). This effect is reversible and suggests reduced aromatic π–π interactions between gelator molecules upon warming. To evaluate the role of the annulated benzo moiety in salts **1**, we included their homologous imidazolium halides **2** in our gelation study. However, no gel formation could be observed in any of the selected solvents under similar testing conditions, even if the gelator concentration was increased to >5 wt%. This result clearly demonstrates the efficiency of π stacking resulting from the benzo substitution pattern of bisbenzimidazolium halides **1.**

The structures and the dimensions of the gel network of **1a–c**/*n*BuOH have been studied by small-angle X-ray scattering (SAXS).[5,11] The SAXS patterns confirm that the crystalline columnar structure of **1a** is preserved in the gels, giving a characteristic distance within the columns of 3.65 nm for **1a**/*n*BuOH, 2.80 nm for **1b**/*n*BuOH, and 2.37 nm for **1c**/*n*BuOH, as derived from the intense peaks at $2\theta = 2.42$, 2.65, and 3.15°, respectively (Figure 5). The distance between the

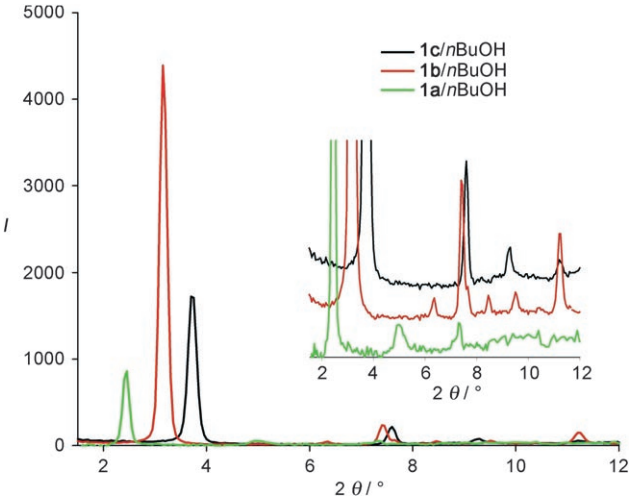
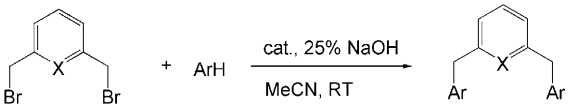


Figure 5. X-ray scattering patterns of gels of 5 wt% **1a**/*n*BuOH, **1b**/*n*BuOH, and **1c**/*n*BuOH gels (after subtraction of background from the solvent). In the inset, the curves are amplified and vertically shifted for clarity.

columns in the crystal of **1a** (4.15 nm, Figure 3d) is slightly larger than that found for gel **1a**/*n*BuOH. This indicates that alcohols with longer alkyl chains improve the linkage of gelator molecules, strengthening the van der Waals interactions between the columns, which results in gel formation (Table 1). The SAXS study reveals a significant counterion effect which, in comparison to bromide salt **1a**, results in a more efficient gelation by the iodide homologue **1b**. A repeating distance of 3.65 nm observed for gel **1a**/*n*BuOH is reduced to 2.8 nm for gel **1b**/*n*BuOH which, moreover, is characterized by a more complex aggregation pattern, as indicated by additional peaks in the range of larger scattering angles (Figure 5, insert).

Although metallogels[12] formed by LMMGs have been applied as catalysts in the oxidization of benzylic alcohol[13] and in a double Michael addition reaction,[7a] no example of a metal-free catalysis in a gel has been reported so far. We turned our attention to phase-transfer catalysts (PTC),[14] and in particular to 2,6-bis[(benz)imidazolylmethyl]pyridines **3a–d**, which are key precursors of NHC complexes[15] and cationic cyclophanes.[16] Recently, quaternary ammonium salts and pyridinophanes have been applied as PTCs to the synthesis of **3a,c** under standard conditions (25% aqueous NaOH solution and MeCN at room temperature) resulting in low yields (up to 30% for **3c**) after longer reaction times (> 12 h).[16a] We have found that gels **1a,b**/MeCN significantly accelerate these phase-transfer reactions (Table 2).

Table 2: Phase-transfer catalyzed N-alkylation of benzimidazole, benzotriazole and imidazole.



3a: X = N, Ar = Benzimidazole
3b: X = N, Ar = Benzotriazole
3c: X = N, Ar = Imidazole
3d: X = CH, Ar = Benzimidazole

Entry	Catalyst	Time [h][a]	Product	Yield [%][b]
1	**1a (1b)**[c]	50	**3a**	60 (61)
2	–	50	**3a**	60
3	gel **1b**/MeCN (5 wt%)	3	**3a**	89
4	gel **1a**/MeCN (5 wt%)	5	**3a**	92
5	gel **1b**/MeCN (5 wt%)	3	**3b**	59
6	gel **1a**/MeCN (5 wt%)	6	**3c**	67
7	gel **1b**/MeCN (5 wt%)	5	**3c**	63
8	gel **1b**/MeCN (5 wt%)	3	**3d**	90

[a] Determined by GC-MS and TLC. [b] Yield of isolated product. [c] Saturated solution of **1a** or **1b** in MeCN (10 mL).

Owing to the low solubility of the bisbenzimidazolium salts in acetonitrile, saturated solutions of **1a,b** do not accelerate the formation of **3a** relative to a blank test (50 h/RT; Table 2, entries 1 and 2). When, however, gel **1b**/MeCN was applied as a PTC, the reaction was completed within three hours, with an 89% yield of isolated product (Table 2, entry 3). Replacing iodide with bromide slows down the reaction (Table 2, entry 4), indicating a counterion effect. Stirring is required for the phase-transfer catalysis, which leads to a partial degradation of the gel network into gel fibers, which remain visible during the reaction. Because of their insolubility, they can be recovered after filtration and reused as a catalyst after regelation with acetonitrile. The procedure has been extended to the synthesis of benzotriazole and imidazol analogues **3b,c** (Table 2, entries 5–7), affording slightly lower yields. Dialkylation of *m*-dibromoxylene gave **3d** in a 90% yield (Table 2, entry 8); similar results were obtained with *o*- and *p*-dibromoxylene.[8]

These results indicate that the gel fibers obtained from benzimidazolium salts **1a,b** are quite efficient in phase-transfer N-alkylations. We propose that the fibers formed after partial degradation of the gel may increase the specific surface area of the catalytic centers. In addition, long N-alkyl chains force the pincer core towards the organic solvent/water interface. The multiple catalytic centers in the fiber aggregates, evident in Figure 3c, may explain the efficiency of the catalyst.

In conclusion, simply structured benzimidazolium halides **1a–d** present a novel type of LMMGs, which not only efficiently gelate a variety of polar protic and aprotic solvents even in concentrations as low as 0.5 wt%, but are also well-suited as PTCs for N-alkylation, as demonstrated for (benz)-imidazole and benzotriazole. A packing model derived from single-crystal X-ray diffraction of gelator **1a** suggests that π stacking between the (hetero)aromatic rings, hydrogen bonding, and van der Waals interactions between the alkyl chains are responsible for the self-assembly in the gelation process. This hypothesis was confirmed by both X-ray analysis, SAXS, and temperature-dependent ^{1}H NMR studies, and by a comparison of the aggregation behavior of homologous imidazolium and benzimidazolium salts. The role as metal-free catalysts extends the scope of benzimidazolium salts beyond their application as ionic solvents and carbene precursors.

Experimental Section

Synthesis of benzimidazolium halides (**1**): A mixture of 2,6-bis(benzimidazol-1-yl)pyridine[8] (622 mg, 2 mmol) and haloalkane RX (4 mmol) was stirred neat at 160 °C for 30 h. After cooling, the mixture was dissolved in $CHCl_3$ (50 mL), and then Et_2O (250 mL) was added. The crude product was purified by reprecipitation from $CHCl_3/Et_2O$ to give a yellow solid **1** in almost quantitative yield, which was shown to be pure by NMR spectroscopy. For **1a**: ^{1}H NMR ([D$_6$]DMSO, 500 MHz, 358 K): $\delta = 10.25$ (s, 2H), 8.17 (t, $J = 8.0$ Hz, 1H), 7.87 (dt, $J = 8.3$ and 1.0 Hz, 2H), 7.85 (d, $J = 8.0$ Hz, 2H), 7.68 (dt, $J = 8.3$ and 1.0 Hz, 2H), 7.25 (ddd, $J = 8.0$, 7.5, and 1.0 Hz, 2H), 7.19 (ddd, $J = 8.0$, 7.5, and 1.0 Hz, 2H), 4.14 (t, $J = 7.5$ Hz, 4H), 1.54 (quintet, $J = 7.5$ Hz, 4H), 0.92 (quintet, $J = 7.8$ Hz, 4H), 0.83 (quintet, $J = 7.5$ Hz, 4H), 0.65–0.79 (m, 44H), 0.30 ppm (t, $J = 7.0$ Hz, 6H). ^{13}C NMR ([D$_6$]DMSO, 125 MHz, 298 K): $\delta = 147.23$, 145.44, 143.53, 132.65, 130.58, 128.88, 128.36, 119.19, 116.47, 115.15, 48.57, 32.04, 29.78, 29.72, 29.63, 29.40, 29.37, 29.31, 26.73, 22.78, 14.55 ppm. HRMS (MALDI, DCTB): $m/z = 840.5536$ $[M-Br]^+$ (found), 840.5513 (calcd). Elemental analysis (%) calcd for $C_{51}H_{79}Br_2N_5 \cdot H_2O$ (940.0297): C 65.16, H 8.69, N 7.45; found: C 65.38, H 8.39, N 7.49.

Analytical data for **1b–e** are compiled in the Supporting Information.[8]

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