New 4′-Functionalized 2,2′:6′,2′′-Terpyridines for Applications in Macromolecular Chemistry and Nanoscience

Philip R. Andres,[a] Ralph Lunkwitz,[b] Gunther R. Pabst,[b] Karlheinz Böhn,[b] Daan Wouters,[a] Stefan Schmatloch,[a] and Ulrich S. Schubert*[a]

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The well-known reaction of 4′-chloro-2,2′:6′,2′′-terpyridine with alkoxide nucleophiles leads to 4′-functionalized 2,2′:6′,2′′-terpyridines. This reaction allows the easy introduction of different functional groups onto the terpyridine at the 4′-position, i.e. opposite to the metal binding site, in one reaction step. Among the functionalized 2,2′:6′,2′′-terpyridines reported here are amines (including chiral examples), carboxylic acids, simple alkoxy-chain terpyridines with different chain lengths, and a stilbene-functionalized terpyridine. Moreover, the synthesis of two important already known substances was significantly improved. One example of a sequential functionalization of the (aminopentoxy)terpyridine with a dithiolane functionality is also reported. For two of the alkyl-chain-functionalized terpyridines, single-crystal X-ray crystallographic data were obtained. Finally, ordered monolayers of alkyl-substituted terpyridines on HOPG were visualized using STM.

Introduction

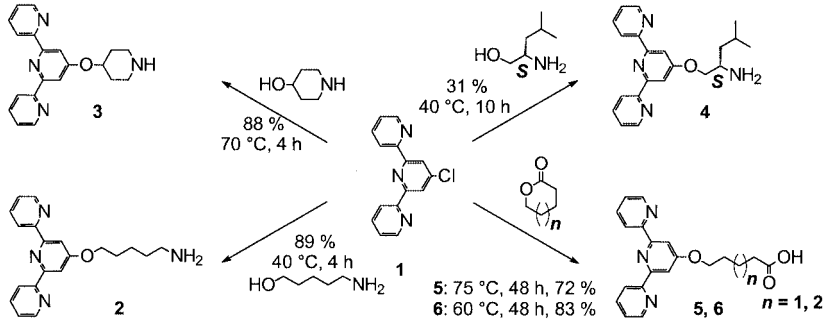
Terpyridines, which form metal complexes with a variety of transition metal ions,[1] have many potential applications in fields such as macromolecular chemistry, nanoscience, biochemistry and photophysics. In particular, 2,2′:6′,2′′-terpyridine and its derivatives have been used as building blocks for novel supramolecular structures, such as double helicates,[2] dendrimers,[3] micelles,[4] metallo-supramolecular polymers[5] and others.[6] Terpyridines are also used in nanoscience, for example, in the formation of ordered architectures on surfaces[7] or functional molecular devices.[8] Biochemical applications include the potential use of terpyridine complexes as sensors in tumor research[9] and as DNA/RNA binding agents.[10] Concerning photophysical applications, ruthenium(II) complexes in particular have received much attention recently in solar cell[11] and luminescent device[12] applications. Also, the immobilization of terpyridines onto polymer resins could prove to be of importance in fields such as catalysis.[13] In particular, the use of 2,2′:6′,2′′-terpyridines functionalized in the 4′-position is of great interest in the above-described fields.[3c,5a,10b]

[a] Laboratory of Macromolecular Chemistry and Nanoscience, Center for Nanomaterials, Eindhoven University of Technology and Dutch Polymer Institute,
P. O. Box 513, 5600 MB Eindhoven, The Netherlands
Fax: (internat.) + 31-40/247-4186
E-mail: u.s.schubert@tue.nl
Center for Nanoscience, LMU München,
Geschwister-Scholl-Platz 1, 80539 München, Germany
[b] BASF Aktiengesellschaft,
67056 Ludwigshafen, Germany

For all the above-mentioned applications, easy access to differently functionalized 2,2′:6′,2′′-terpyridines on a large scale and high yields is a prerequisite.[14] Herein we present the synthesis of a variety of terpyridines functionalized in the 4′-position, by the well-known nucleophilic substitution reaction of alkoxides (alkoxides, formed in situ under the strong basic conditions − KOH/DMSO − are, in contrast to the corresponding alcohols, good nucleophiles) with 4′-chloro-2,2′:6′,2′′-terpyridine,[15] first described by Newkome et al.[16] It should be mentioned that the synthesis of such 4′-ether-bridge-functionalized terpyridines can also be carried out starting from the precursor of 4′-chloro-2,2′:6′,2′′-terpyridine, the 2,2′:6′,2′′-terpyridin-4′(1′*H*)-one, which, in contrast, requires an electrophile as functionalizing reactant.[14,17] Two of the amine- and carboxy-functionalized terpyridines presented here have already been applied to the construction of dendritic structures[16] or the functionalization of coiled-coil peptide sequences.[18] Furthermore, the alkyl-chain-functionalized terpyridines presented here formed ordered two-dimensional structures on HOPG (Highly Ordered Pyrolytic Graphite), which were investigated by STM.[19] The combination of a terpyridine moiety and a thiol functionality in one molecule seems especially appealing for the construction of metallo-supramolecular structures including gold surfaces or colloids.[20] Also, the dithiolane moiety is known to bind to gold, in some cases resulting in the formation of SAMS.[21]

Results and Discussion

The introduction of different functionalities into the 4′-position of the 2,2′:6′,2′′-terpyridine in one reaction step,



Scheme 1. Synthesis of 4′-(aminoalkoxy)- and 4′-(carboxyalkoxy)-functionalized 2,2′:6′,2′′-terpyridines; all reactions were performed in DMSO/KOH

starting from 4′-chloro-2,2′:6′,2′′-terpyridine (**1**), is described. This starting material was first reported by Ward et al.[22] and has recently been synthesized on a large scale.[23] Utilizing the base-catalyzed nucleophilic substitution of the chloro function with functional alkoxides in an aprotic medium, such as DMSO, led to the formation of 4′-functionalized terpyridines with an alkoxy spacer. Several amino- and carboxy-functionalized 2,2′:6′,2′′-terpyridines were prepared by the reaction of the corresponding alkoxides with 4′-chloro-2,2′:6′,2′′-terpyridine (**1**, Scheme 1). The amino-functionalized terpyridines were obtained by addition of the amino alcohols to a KOH/basic DMSO suspension, and the subsequent addition of 4′-chloro-2,2′:6′,2′′-terpyridine.[1] Amines **2** and **3** were isolated in yields of 89 and 88%, respectively. In the case of **2**, which is known in the literature,[16] the yield was increased and the workup procedure simplified. Lowering the reaction temperature still resulted in 100% conversion after a reaction time of 4 h. Moreover, decomposition of the starting material or formation of a bis(terpyridine)-functionalized material was observed in this case. Simple precipitation of the product by pouring the reaction mixture into a tenfold excess of water, followed by filtration and chemical and physical drying, yielded the pure product.

We recently developed a new route for the functionalization of the 4′-chloroterpyridine **1** with carboxyalkoxy chains. Utilizing the same strategy as described above, but taking advantage of the ring-opening reaction of lactones to give in situ formation of alkoxide nucleophiles under the basic reaction conditions, the 4′-(carboxyalkoxy)-functionalized terpyridines **5** and **6** with different alkyl spacer lengths were obtained (Scheme 1). For the final purification of these compounds, recrystallization from THF was found to be most convenient. The reaction conditions of the experiments and melting points of the products are listed in Table 1. The reaction time given represents the time of the reaction until at least 95% conversion of the 4′-chloro-2,2′:6′,2′′-terpyridine (**1**) has been reached (as shown by ^{1}H NMR spectroscopy).

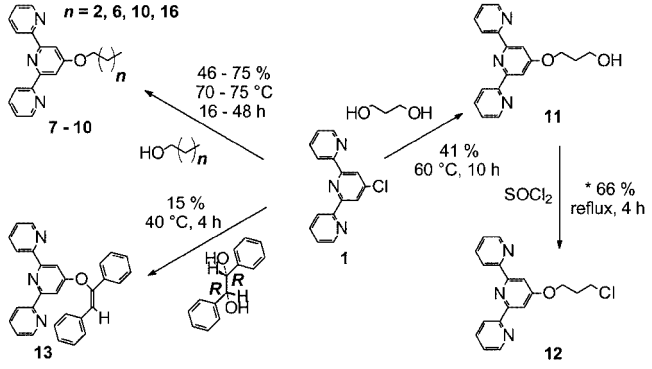
As expected, higher melting points were observed for the (carboxyalkyloxy)terpyridines **5** and **6**, as well as for the more rigid piperidine-functionalized terpyridine. Having an alkyl chain or even a branched chain between the amine and the terpyridine decreases the melting point from **3** (181 °C) to **2** (104 °C) to **4** (liquid at room temperature). Concerning the reaction times and the reaction temperatures, conditions of a reaction time of 4 h is required at 40 °C for the full conversion of the unbranched 5-amino-1-pentanol to the (aminopentoxy)terpyridine **2**. Increasing values for reaction temperature and/or reaction time are required for the secondary alcohol 4-hydroxypiperidine (which leads to **3**) and the sterically more hindered L-leucinol (which leads to **4**). The longest reaction times of 48 h were required for the ring opening of the lactones (leading to **5** and **6**). For all of these compounds yields of 70−90% could be obtained except for the chiral amine **4** (31%). The

Table 1. Reaction data of the functionalized terpyridines (terpyridine−O−X)

	X	Reagent	Time [h]	Temp. [°C]	M.p. [°C]	Yield [%]	Literature yield [%]
2	pentyl-NH_2	5-amino-1-pentanol	4	40	104	89	72[14], 75[13]
3	piperidin-4-yl	4-hydroxypiperidine	4	70	181	88	–
4	(*S*)-2-amino-4-methylpentyl	L-leucinol	10	40	–	31	–
5	pentyl-COOH	ε-caprolactone	48	60	205	83	65[13]
6	butyl-COOH	δ-valerolactone	48	75	175	72	–
7	butyl	1-butanol	16	70	104	46	–
8	octyl	1-octanol	21	70	97	59	–
9	dodecyl	1-dodecanol	48	70	97	51	–
10	octadecyl	1-octadecanol	48	75	99	75	–
12	propyl-Cl	$SOCl_2$	5	reflux	105	66	–
13	stilbene	(*R*,*R*)-(+)-hydrobenzoin	4	40	192	15	–
14	*N*-pentylthioctamide	DL-thioctic acid	10	room temp.	99	35	–

explanation for the low yield in the latter case can be found in the high water solubility of the product; thus, **4** cannot be precipitated in water, and its purification required extensive column chromatography. However, a clear increase in the yields for the already reported (aminopentoxy)terpyridine **2** from 75 to 89% and for the (carboxypentoxy)terpyridine **5** from 65 to 83% were observed.

Furthermore, the alkoxy-functionalized ligands **7**−**10**, the (chloroalkoxy)-functionalized terpyridine **12**, as well as the stilbene-functionalized terpyridine **13** (Scheme 2) were synthesized starting from the chloroterpyridine **1**.



Scheme 2. Synthesis of several alkoxy-, chloroalkoxy- and stilbeneoxy-functionalized 2,2′:6′,2″-terpyridines; all reactions were performed in DMSO/KOH (except *)

Compounds **7**−**10** were obtained by the reaction of the corresponding alkanols with **1**. Purification could be achieved through recrystallization from ethyl acetate/hexane mixtures, leading to crystalline compounds. For two of the compounds, the *n*-butoxyterpyridine **7** and the *n*-dodecanoxyterpyridine **9**, single crystals suitable for X-ray crystallographic investigations were obtained (Figure 1).

For both compounds the terpyridine rings lie nearly in one plane, in the thermodynamically favoured *trans-trans* conformation (with respect to the nitrogen atoms). However, the crystal structures do show differences based on the length of the alkoxy chain. One difference becomes apparent when comparing the torsion angles of O(19)−C(20)−C(21)−C(22) for the two compounds. This angle is −159.0° for the *n*-butoxyterpyridine **7**, and 176.1° for the *n*-dodecyloxyterpyridine **9**. Also, the torsion angle for C(20)−C(21)−C(22)−C(23) shows a significant difference, being −164.8° for **7** and −178.2° for **9**. This difference is caused by the stacking of the longer alkyl chains of **9**, which leads to a decrease in torsion in the alkyl chain. Such stacking does not occur in the crystal for the short alkyl chain of **7**. In this manner, the dodecyl chain dominates the structure in the crystal for compound **9**, whereas the terpyridine moiety dominates the structure in the crystal for compound **7**. Accordingly, the terpyridine rings of **9** are more twisted [C(5)−C(6)−C(12)−N(7) −10.6°] than those of **7** [C(5)−C(6)−C(12)−N(7) −2.9°] and the bond between the sp^2 carbon atoms which connect the rings is slightly elongated for **9** [C(6)−C(12) 150.3 pm] compared to **7** [C(6)−C(12) 149.2 pm]. Moreover, self-assembled monolayers of compounds **9** and **10** on highly ordered pyrolytic graphite (HOPG) have been imaged by scanning tunnelling microscopy (Figure 2). In the inset of Figure 2, a high-resolution image of **9** is shown with an overlay of a geometry-optimized model. The match between the two is striking, and illustrates the geometry in the crystal. A more detailed description can be found in ref.[19]

Additionally, the syntheses of the stilbene-functionalized terpyridine **13**, utilizing the same chemistry as described above, and of the (chloropropoxy)terpyridine **12** and the thiolane-functionalized terpyridine **14** are reported. The latter two compounds were obtained through sequential functionalization of the (hydroxypropoxy)terpyridine **11** and the (aminopentoxy)terpyridine **2**, respectively. The stilbene-functionalized terpyridine **13** could prove to be useful through the combination of photophysically interesting moieties such as terpyridine complexes with stilbene and/or its copolymers. Treatment of 4′-chloro-2,2′:6′,2′′-terpyridine (**1**) with 0.5 equiv. of (*R*,*R*)-dihydrobenzoin does not lead to a ditopic bis(terpyridyl) ligand, but partially to the stilbene-functionalized terpyridine **13**. The reaction was stopped before full conversion was reached, in order to avoid by-product formation or degradation. The appearance of the typical absorption shoulder at 320 nm as well as only one signal for the double-bond proton of the stilbene moiety in the ^{1}H NMR spectrum indicate the formation of the thermodynamically favoured *trans* isomer. A new terpyridine functionalized with a halopropoxy, here a chloropropoxy, which could serve as an important intermediate for further terpyridine functionalization, was obtained by a functional group interconversion from the known hydroxyalkoxy-functionalized terpyridine **11**, itself obtained through reaction of 4′-chloro-2,2′:6′,2′′-terpyridine (**1**) with an excess of propane-1,3-diol.[24] Reaction of **11** in refluxing $SOCl_2$ led to the (chloropropoxy)terpyridine **12**, which, after recrystallization, was obtained as pure compound in 66% yield. An approach towards a metal-surface-active terpyridine was made by functionalizing the above-mentioned aminoterpyridine **2** by reaction with racemic DL-thioctic acid utilizing the well-known DCC method in order to yield the dithiolane-functionalized terpyridine **14** in 35% yield (Scheme 3). The pure product was obtained after column chromatography and repeated recrystallization from diethyl ether. These measures of purification were necessary in order to separate the product from the main by-product, dicyclohexylurea.

Applying other coupling methods, which, for example, include activation with CDI (*N*,*N*′-carbonyldiimidazole), could increase the yield. A useful tool for the detection of such higher mass molecules, and possible higher molecular weight by-products, is MALDI-TOF mass spectrometry. Figure 3 shows the spectrum of pure **14**. Apart from the molecule isotope distribution plus hydrogen from the matrix dithranol, the only major detected species is the molecule plus sodium, which is typical for MALDI-TOF-MS. A good proof for the detection of the desired molecule is

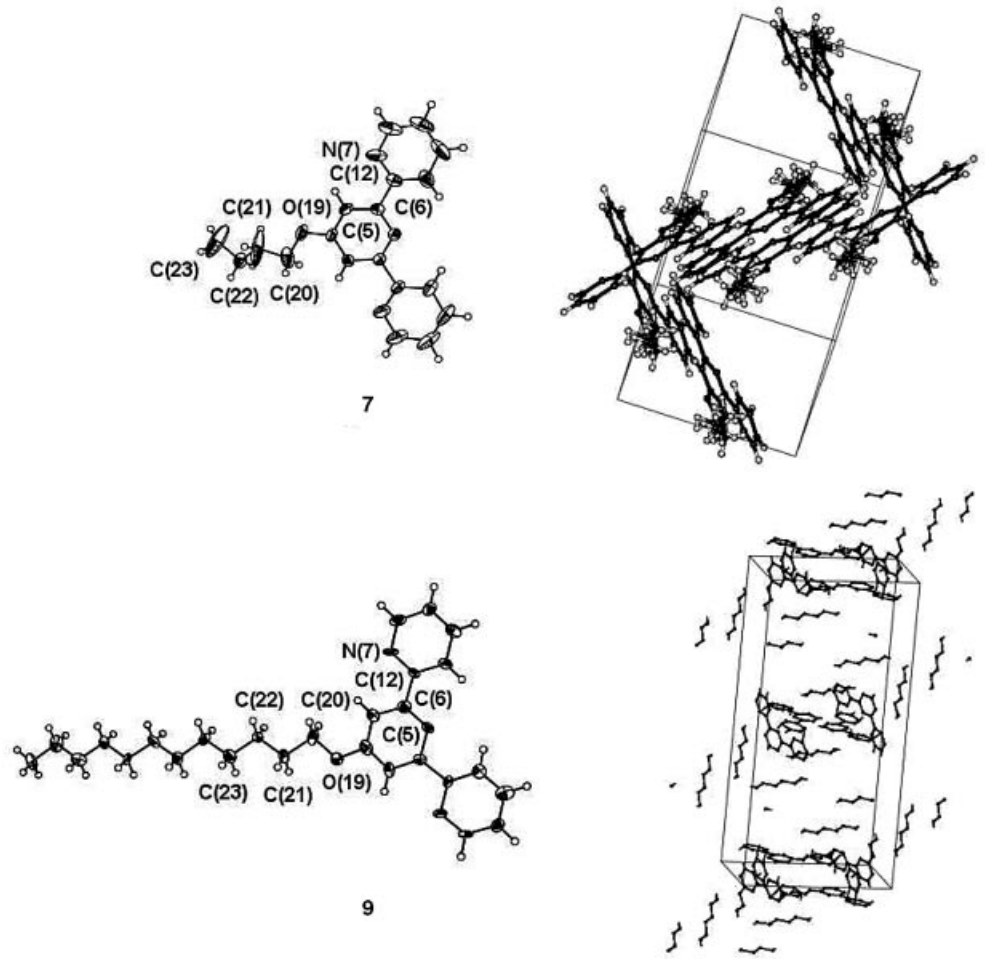


Figure 1. Single-crystal X-ray structures of **7** and **9**

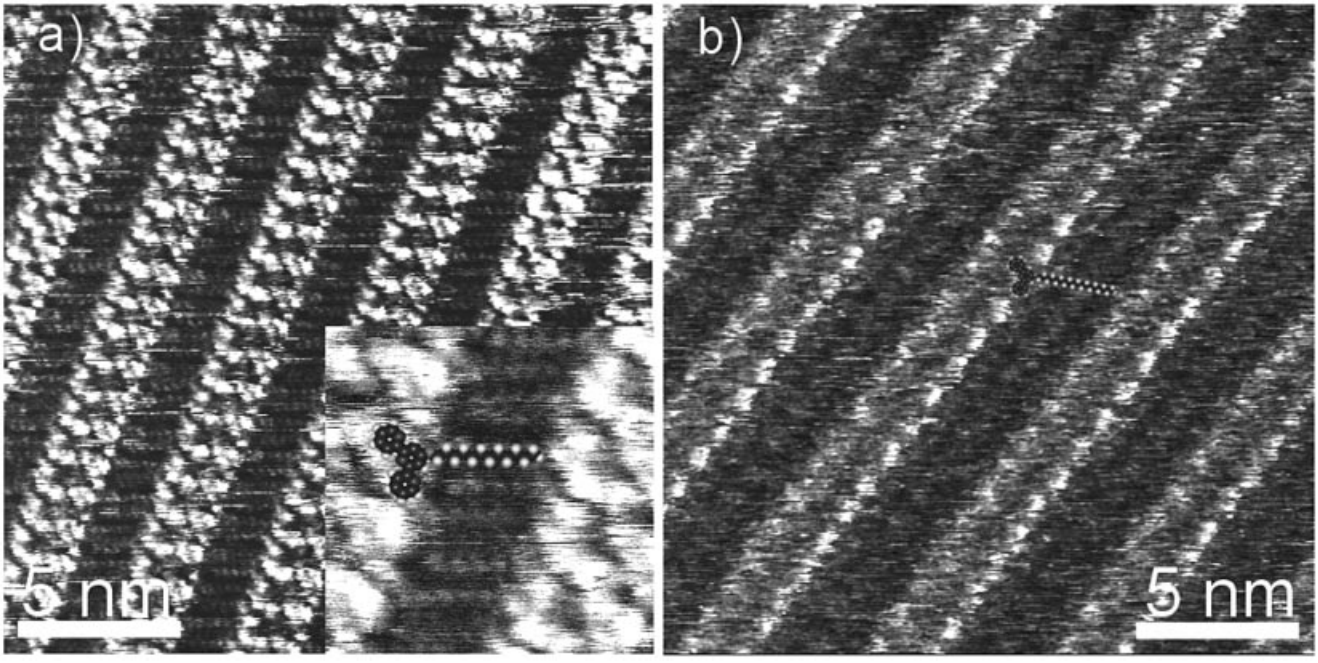
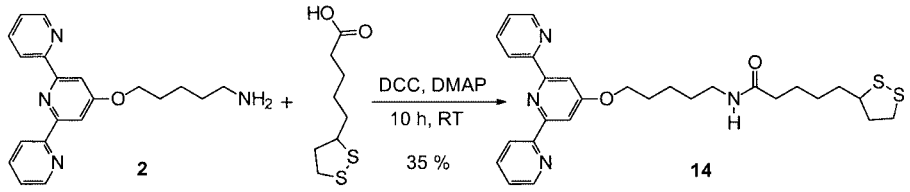


Figure 2. a) STM-image of a self-assembled 2D monolayer of compound **9** on HOPG; inset shows a high-resolution image with an overlay of a geometry-optimized model; b) STM image of a self-assembled 2D monolayer of compound **10** (see also ref.[19])



Scheme 3. Synthesis of the dithiolane-functionalized 2,2′:6′,2′′-terpyridine **14**

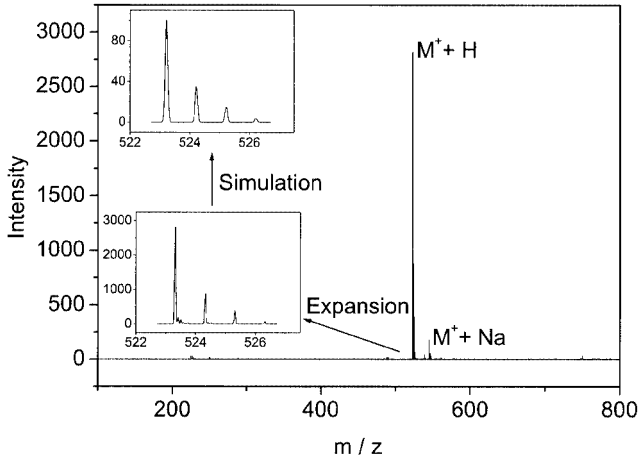


Figure 3. MALDI-TOF-MS of **14**

also provided by the simulation of the isotopic distribution, which is shown in the top inset.

Conclusion

Starting from 4′-chloro-2,2′:6′,2′′-terpyridine (**1**), a series of new 2,2′:6′,2′′-terpyridines linked via an ether bridge to different functional groups was synthesized. In this way, terpyridines bearing amino, carboxylic acid, alkyl chain and stilbene functionalities were obtained. A new, convenient route for the introduction of alkylcarboxylic acids in the 4′-position of the terpyridine has been established. This takes advantage of the in situ ring opening of lactones under the basic reaction conditions and the subsequent reaction of the resulting alkoxide with the chloroterpyridine. The sequential functionalization of the amine-functionalized terpyridine **2** with DL-thioctic acid led to a dithiolane-functionalized terpyridine **14**. Two of the 4′-alkoxy-functionalized terpyridines gave single crystals suitable for X-ray crystallographic analysis, the results of which demonstrated the influence of different alkyl chain lengths on the crystal structure. Ordered 2D arrays of **9** and **10** on HOPG were also imaged by STM. The easy availability of all of the reported compounds opens new possibilities for the design of different types of 4′-functionalized terpyridine building blocks with different alkyl spacer lengths. As a result, tailor-made ligands for macromolecular and nanoscience applications are accessible.

Experimental Section

General Remarks: Standard chemicals were obtained from Sigma−Aldrich. 4′-Chloro-2,2′:6′,2′′-terpyridine was synthesized by BASF AG (see also ref.[23]). ^{1}H and ^{13}C NMR were recorded with a Varian Mercury 400 spectrometer and the chemical shifts were calibrated to the solvent peaks. For clarity, the carbon and hydrogen atoms of the alkyl spacers are numbered using greek symbols starting from the first carbon atom at the functionality and ending at the carbon next to the 4′-ether function at the terpyridine. UV/Vis spectra were recorded with a Perkin−Elmer Lambda-45 (1-cm cuvettes). MALDI-TOF mass spectra were recorded with a Perseptive Biosystems Voyager-DE STR Biospectrometry and EIMS were obtained from a Shimadzu GCMS-QP5000. Elemental analyses were measured with a Perkin−Elmer Series II 2400 and melting points were obtained with a Büchi Melting Point B-540. STM imaging was performed at the solid/liquid interface (liquid: phenyloctane) on a multimode scanning probe microscope from Digital Instruments (DI, Santa Barbara, CA, USA).

5-(2,2′:6′,2′′-Terpyridin-4′-yloxy)pentylamine (2): 5-Aminopentanol (9.4 g, 91 mmol) was added dropwise to a stirred suspension of powdered KOH (2.82 g, 50.3 mmol) in DMSO (250 mL) at 40 °C. After 20 min, 4′-chloro-2,2′:6′,2′′-terpyridine (**1**, 5.58 g, 20.8 mmol) was added. The mixture was stirred at 40 °C for 2.5 h and then poured into deionized water (1.75 L). The aqueous phase was removed by filtration and the product was washed with deionized water and dried in vacuo, yielding **2** as a light yellow solid (6.20 g, 89%, ref.[14] 71%, ref.[13] 75%). M.p. 104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (s, 2 H, NH_2), 1.52−1.57 (m, 4 H, $H_{\beta,\gamma}$), 1.87 (tt, J = 5.91, 6.10 Hz, 2 H, H_δ), 2.73 (t, J = 6.10 Hz, 2 H, H_α), 4.23 (t, J = 6.10 Hz, 2 H_ε), 7.32 (ddd, J = 1.0, 4.6, 7.2 Hz, 2 H, $H_{5,5''}$), 7.83 (ddd, J = 4.9, 7.2, 7.2 Hz, 2 H, $H_{4,4''}$), 8.03 (s, 2 H, $H_{3',5'}$), 8.60 (d, J = 7.2 Hz, 2 H, $H_{3,3''}$), 8.69 (d, J = 4.6 Hz, 2 H, $H_{6,6''}$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 23.4 (C_γ), 28.9 (C_β), 33.6 (C_δ), 42.2 (C_α), 68.1 (C_ε), 107.4 ($C_{5,5''}$), 121.3 ($C_{4,4''}$), 123.8 ($C_{3,3''}$), 136.8 ($C_{3',5'}$), 149.0 ($C_{6,6''}$), 156.2 ($C_{2,2''}$), 157.1 ($C_{2',6'}$), 167.3 ($C_{4'}$) ppm. MALDI-TOF-MS (matrix: dithranol): m/z = 335 [MH$^+$]. EIMS (70 eV): m/z = 334 [M$^+$]. $C_{20}H_{22}N_4O$ (334.42): calcd. C 71.83, H 6.63, N 16.75; found C 71.70, H 6.27, N 16.80.

4′-(2-Piperidin-4-yloxy)-2,2′:6′,2′′-terpyridine (3): 2-(Piperidin-4-yl)ethanol (0.823 g, 6.37 mmol) was added to a stirred suspension of powdered KOH (297 mg, 5.29 mmol) in DMSO (60 mL) at 70 °C. After 20 min, 4′-chloro-2,2′:6′,2′′-terpyridine (**1**, 0.56 g, 2.11 mmol) was added. The mixture was stirred at 70 °C for 4 h and then poured into deionized water (600 mL). The aqueous phase was removed by filtration and the product was washed with deionized water and dried in vacuo, yielding **3** as a white solid (664 mg, 88%). M.p. 181 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 1 H, NH), 1.75 (m, 4 H, $H_{\beta1}$), 2.07 (m, 2 H, $H_{\beta2}$), 2.80 (m, 2 H, $H_{\alpha1}$), 3.15 (m, 2 H, $H_{\alpha2}$), 4.78 (m, 2 H, H_γ), 7.33 (ddd, J =

1.0, 4.5, 7.1 Hz, 2 H, $H_{5,5''}$), 7.83 (ddd, J = 4.9, 7.2, 7.2 Hz, 2 H, $H_{4,4''}$), 8.01 (s, 2 H, $H_{3',5'}$), 8.60 (d, J = 7.2 Hz, 2 H, $H_{3,3''}$), 8.72 (d, J = 4.5 Hz, 2 H, $H_{6,6''}$) ppm. ^{13}C NMR (300 MHz, [D$_8$]THF): δ = 32.1, 43.7 (C_α, C_β), 72.9 (C_γ), 108.2, 121.3, 123.8, 136.8, 149.0, 156.2, 165.9 ($C_{2,2''}$, $C_{3,3''}$, $C_{4,4''}$, $C_{5,5''}$, $C_{6,6''}$, $C_{2',6'}$, $C_{3',5'}$, $C_{4'}$) ppm. EIMS (70 eV): m/z = 332 [M$^+$]. $C_{36}H_{32}N_6S_2$ (332.40): calcd. C 72.27, H 6.06, N 16.85; found C 72.20, H 6.15, N 16.90.

3-Methyl-1-[(*S*)-(2,2′:6′,2′′-terpyridin-4′-yloxy)methyl]butylamine (4): (*S*)-Leucinol (1.31 g, 11.2 mmol) was added dropwise to a stirred suspension of powdered KOH (377 mg, 6.72 mmol) in DMSO (50 mL) at 30 °C. After 30 min, 4′-chloro-2,2′:6′,2′′-terpyridine (**1**, 600 mg, 2.24 mmol) was added. The mixture was stirred at 30 °C for 10 h and then poured into deionized water (500 mL). The aqueous phase was extracted with dichloromethane (DCM, 3 × 150 mL), the organic fractions were combined, and the solvent was evaporated to give the crude product as a yellow oil. Further purification was carried out by column chromatography (Alox N, eluent DCM, gradient with MeOH 5% → 10%). After removal of the solvent in vacuo, **4** was isolated as a light-yellow oil (240 mg, 31%). R_f = 0.58 (alox N, CH_2Cl_2/MeOH, 92:8). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (m, 6 H, 2 CH_3,) 1.37 (m, 2 H, CHCH_2CH), 1.50 (b, 2 H, NH_2), 1.81 [m, 1 H, $CH_2CH(CH_3)_2$], 3.30 (m, 1 H, CHNH$_2$), 3.96, 4.17 (2 dd, J = 7.6, 8.9, J = 3.8, 9.0 Hz, 2 H, OCH_2), 7.32 (ddd, J = 1.1, 5.0, 4.2 Hz, 2 H, $H_{5,5''}$), 7.84 (ddd, J = 1.8, 5.0, 7.3 Hz, 2 H, $H_{4,4''}$), 8.01 (s, 2 H, $H_{3',5'}$), 8.61 (d, J = 7.3 Hz, 2 H, $H_{3,3''}$), 8.70 (d, J = 4.2 Hz, 2 H, $H_{6,6''}$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 22.1, 23.3, 24.7, 43.1, 48.5 ($C_{aliph.}$), 73.8 (OCH$_2$), 107.3 ($C_{5,5''}$), 121.3 ($C_{4,4''}$), 123.8 ($C_{3,3''}$), 136.8 ($C_{3',5'}$), 149.0 ($C_{6,6''}$), 156.0 ($C_{2,2''}$), 157.1 ($C_{2',6'}$), 167.1 ($C_{4'}$) ppm. EIMS (70 eV): m/z = 348 [M$^+$]. $C_{21}H_{24}N_4O$ (348.44): calcd. C 72.39, H 6.94, N 16.08; found C 72.06, H 6.76, N 15.89.

5-(2,2′:6′,2′′-Terpyridin-4′-yloxy)pentanoic Acid (5): δ-Valerolactone (0.52 g, 5.2 mmol) was added dropwise to a stirred suspension of powdered KOH (0.74 g, 11 mmol) in DMSO (50 mL) at 75 °C. After 30 min, 4′-chloro-2,2′:6′,2′′-terpyridine (**1**, 696 mg, 2.60 mmol) was added. The mixture was stirred at 75 °C for 48 h and then poured into deionized water (175 mL). Concentrated hydrochloric acid was added dropwise to the transparent solution until precipitation of a white solid was observed (pH ≈ 6). The aqueous phase was then removed by filtration, and the crude product was washed with ethanol and dried in vacuo, yielding **5** as a white solid (654 mg, 72%). M.p. 205 °C. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 1.78 (m, 2 H, H_δ), 1.87 (m, 2 H, H_γ), 2.32 (t, J = 7.2 Hz, 2 H, H_β), 4.22 (t, J = 6.3 Hz, 2 H, H_ε), 7.29 (ddd, J = 1.2, 4.6, 7.4 Hz, 2 H, $H_{5,5''}$), 7.82 (ddd, J = 1.8, 7.9, 7.9 Hz, 2 H, $H_{4,4''}$), 8.07 (s, 2 H, $H_{3',5'}$), 8.56 (m, 4 H, $H_{3,3''}$, $H_{6,6''}$), 10.65 (b, 1 H, HOOC) ppm. ^{13}C NMR (300 MHz, [D$_8$]THF): δ = 22.7, 29.7 (C_γ, C_δ), 34.1 (C_β), 68.9 (C_ε), 108.2, 111.8, 121.9, 124.8, 137.6, 150.2, 157.3, 158.3 ($C_{2,2''}$, $C_{3,3''}$, $C_{4,4''}$, $C_{5,5''}$, $C_{6,6''}$, $C_{2',6'}$, $C_{3',5'}$, $C_{4'}$), 168.4 (C_α) ppm. MALDI-TOF-MS (matrix: dithranol): m/z = 350 [MH$^+$]. $C_{21}H_{21}N_3O_3$ (349.38): calcd. C 68.75, H 5.48, N 12.03; found C 68.54, H 5.41, N 11.96.

6-(2,2′:6′,2′′-Terpyridin-4′-yloxy)hexanoic Acid (6): ε-Caprolactone (5.97 g, 52.3 mmol) was added dropwise to a stirred suspension of powdered KOH (7.40 g, 132 mmol) in DMSO (50 mL) at 60 °C. After 30 min, 4′-chloro-2,2′:6′,2′′-terpyridine (**1**, 6.96 g, 26.0 mmol) was added. The mixture was stirred at 60 °C for 48 h and then poured into deionized water (1.6 L). Concentrated hydrochloric acid was added dropwise to the transparent solution until precipitation of a white solid was observed (pH ≈ 6). The aqueous phase was then removed by filtration, and the crude product was recrystallized from THF and dried in vacuo, yielding **6** as a white solid (7.85 g, 83%). M.p. 187 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (tt, J = 6.1, 6.7 Hz, 2 H, H_δ), 1.79 (tt, J = 6.7, 6.7 Hz, 2 H, H_γ), 1.91 (tt, J = 6.1, 6.1 Hz, 2 H, H_ε), 2.42 (t, J = 6.7 Hz, 2 H, H_β), 4.27 (t, J = 6.1 Hz, 2 H, H_ζ), 7.35 (ddd, J = 1.1, 3.9, 4.9 Hz, 2 H, $H_{5,5''}$), 7.84 (ddd, J = 1.6, 4.9, 7.3 Hz, 2 H, $H_{4,4''}$), 7.99 (s, 2 H, $H_{3',5'}$), 8.61 (d, J = 7.3 Hz, 2 H, $H_{3,3''}$), 8.70 (d, J = 3.9 Hz, 2 H, $H_{6,6''}$) ppm. ^{13}C NMR (300 MHz, [D$_8$]THF): δ = 26.8, 30.1 (C_γ, C_δ), 34.5 (C_ε), 43.7 (C_β), 69.1 (C_ζ), 108.2, 109.9, 121.9, 124.9, 137.6, 150.2, 157.3, 158.3 ($C_{2,2''}$, $C_{3,3''}$, $C_{4,4''}$, $C_{5,5''}$, $C_{6,6''}$, $C_{2',6'}$, $C_{3',5'}$, $C_{4'}$), 168.4 (C_α) ppm. EIMS (70 eV): m/z = 362 [M$^+$ − H]. $C_{21}H_{21}N_3O_3$ (363.41): calcd. C 69.41, H 5.82, N 11.56; found C 69.07, H 5.79, N 11.50.

4′-Butoxy-2,2′:6′,2′′-terpyridine (7): 1-Butanol (0.33 g, 4.48 mmol) was added to a stirred suspension of powdered KOH (0.628 g, 11 mmol) in anhydrous DMSO (20 mL) at 70 °C. After 30 min, 4′-chloro-2,2′:6′,2′′-terpyridine (**1**, 1.00 g, 3.74 mmol) was added. The mixture was stirred at 70 °C for 16 h and then poured into deionized water (30 mL). After cooling, the mixture was extracted with CH_2Cl_2 (1 × 50 mL, 2 × 25 mL) and the combined organic extracts were dried with Na_2SO_4. The crude product was recrystallized from ethyl acetate/*n*-hexane, yielding **7** as a yellow crystalline solid (0.5 g, 46%). M.p. 103−105 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.45 Hz, 3 H, H_α), 1.53 (m, 2 H, H_β), 1.83 (m, 2 H, H_γ), 4.21 (t, J = 6.6 Hz, 2 H, H_δ), 7.29 (m, 2 H, Ar-H), 7.81 (dt, J = 7.45, 1.75 Hz, 2 H, Ar-H), 8.01 (s, 2 H, Ar-H), 8.69 (d, J = 8.3 Hz, 2 H, Ar-H), 8.69 (d, J = 4.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 13.81 (C_α), 19.18 C_β), 31.10 (C_γ), 67.94 (C_δ), 107.42 (2 Ar-C), 121.33 (2 Ar-C), 123.73 (2 Ar-C), 136.72 (2 Ar-C), 149.01 (2 Ar-C), 156.24 (2 Ar-C), 157.04 (2 Ar-C), 167.37 (Ar-C) ppm. $C_{19}H_{19}N_3O$ (291.37): calcd. C 74.8, H 6.2, N 13.8; found C 74.7, H 6.1, N 13.8.

4′-Octyloxy-2,2′:6′,2′′-terpyridine (8): 1-Octanol (0.58 g, 4.48 mmol) was added to a stirred suspension of powdered KOH (0.628 g, 11 mmol) in anhydrous DMSO (20 mL) at 75 °C. After 30 min, 4′-chloro-2,2′:6′,2′′-terpyridine (**1**, 1.00 g, 3.74 mmol) was added. The mixture was stirred at 70 °C for 21 h and then poured into deionized water (50 mL). After cooling, the mixture was extracted with CH_2Cl_2 (2 × 50 mL, 1 × 25 mL) and the combined organic extracts were dried with Na_2SO_4. The crude product was recrystallized from ethyl acetate/*n*-hexane, yielding **8** as a white crystalline solid (0.8 g, 59%). M.p. 96−98 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.3 Hz, 3 H, H_α), 1.44−1.2 (m, 8 H, $H_{\beta\gamma\delta\varepsilon}$), 1.55−1.45 (m, 2 H, H_ζ), 1.84 (m, 2 H, H_η), 4.21 (t, J = 6.35 Hz, 2 H, H_θ), 7.30 (m, 2 H, Ar-H), 7.83 (dt, J = 7.3, 1.8 Hz, 2 H, Ar-H), 8.0 (s, 2 H, Ar-H), 8.62 (d, J = 7.9 Hz, 2 H, Ar-H), 8.69 (d, J = 4.9 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 14.10 (C_α), 22.68 (Alk-C), 25.98 (Alk-C), 29.07 (Alk-C), 29.25 (Alk-C), 29.30 (Alk-C), 31.82 C_η), 68.24 (C_θ), 107.43 (2 Ar-C), 121.33 (2 Ar-C), 123.73 (2 Ar−C), 136.72 (2 Ar-C), 149.01 (2 Ar-C), 156.25 (2 Ar-C), 157.03 (2 Ar-C), 167.38 (Ar-C) ppm. $C_{23}H_{27}N_3O$ (361.49): calcd. C 76.5, H 7.5, N 11.6; found C 76.2, H 7.4, N 11.6.

4′-Dodecyloxy-2,2′:6′,2′′-terpyridine (9): 1-Dodecanol (0.84 g, 4.48 mmol) was added to a stirred suspension of powdered KOH (0.628 g, 11 mmol) in anhydrous DMSO (20 mL) at 70 °C. After 30 min, 4′-chloro-2,2′:6′,2′′-terpyridine (**1**, 1.00 g, 3.74 mmol) was added. The mixture was stirred at 70 °C for 48 h and then poured into distilled water (30 mL). After cooling, the mixture was extracted with CH_2Cl_2 (1 × 50 mL, 3 × 25 mL) and the combined organic extracts were dried with Na_2SO_4. The crude product was recrystallized from ethyl acetate/*n*-hexane, yielding **9** as a white crystalline solid (0.8 g, 51%). M.p. 96−98 °C. ^{1}H NMR

(500.13 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 3 H, H_α), 1.44−1.2 (m, 16 H, $H_{\beta\gamma\delta\varepsilon\eta\theta\iota\kappa}$), 1.50 (m, 2 H, H_λ), 1.85 (m, 2 H, H_μ), 4.20 (t, *J* = 6.7 Hz, 2 H, H_ν), 7.31 (m, 2 H, Ar-*H*), 7.83 (dt, *J* = 7.9, 1.8 Hz, 2 H, Ar-*H*), 8.01 (s, 2 H, Ar-*H*), 8.61 (d, *J* = 7.3 Hz, 2 H, Ar-*H*), 8.68 (dd, *J* = 5.5, 2.4 Hz, 2 H, Ar-*H*) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 14.12 (C_α), 22.70 (Alk-*C*), 25.97 (Alk-*C*), 29.07 (Alk-*C*), 29.34 (Alk-*C*), 29.36 (Alk-*C*), 29.59 (Alk-*C*), 29.61 (Alk-*C*), 29.65 (Alk-*C*), 29.68 (Alk-*C*), 31.93 (C_μ), 68.25 (C_ν), 107.43 (2 Ar-*C*), 121.33 (2 Ar-*C*), 123.73 (2 Ar-*C*), 136.73 (2 Ar-*C*), 149.01 (2 Ar-*C*), 156.26 (2 Ar-*C*), 157.04 (2 Ar-*C*), 167.39 (Ar-*C*) ppm. $C_{27}H_{35}N_3O$ (417.59): calcd. C 77.7, H 8.4, N 10.1; found C 77.6, H 8.3, N 9.9.

4′-Octadecyloxy-2,2′:6′,2″-terpyridine (10): 1-Octadecanol (1.21 g, 4.48 mmol) was added to a stirred suspension of powdered KOH (0.628 g, 11 mmol) in water-free DMSO (40 mL) at 75 °C. After 30 min, 4′-chloro-2,2′:6′,2″-terpyridine (**1**, 1.00 g, 3.74 mmol) was added. The mixture was stirred at 75 °C for 48 h and then poured into distilled water (50 mL). After cooling, the mixture was extracted with CH_2Cl_2 (1 × 50 mL, 2 × 25 mL) and the combined organic extracts were dried with Na_2SO_4. The crude product was recrystallized from ethyl acetate/*n*-hexane, yielding **10** as a white crystalline solid (1.4 g, 75%). M.p. 98−99 °C. ^1H NMR (500.13 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 3 H, H_α), 1.44−1.20 (m, 28 H, Alk-$H_{\beta\gamma\delta\varepsilon\zeta\eta\theta\iota\kappa lmn\xi o}$), 1.50 (m, 2 H, H_π), 1.85 (m, 2 H, H_ρ), 4.20 (t, *J* = 6.7 Hz, 2 H, H_ς), 7.31 (m, 2 H, Ar-*H*), 7.83 (dt, *J* = 7.9, 1.8 Hz, 2 H, Ar-*H*), 8.01 (s, 2 H, Ar-*H*), 8.61 (d, *J* = 7.3 Hz, 2 H, Ar-*H*), 8.68 (dd, *J* = 5.5, 2.4 Hz, 2 H, Ar-*H*) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 14.12 (C_α), 22.71 (Alk-*C*), 25.99 (Alk-*C*), 29.08 (Alk-*C*), 29.39 (Alk-*C*), 29.61 (Alk-*C*), 29.63 (Alk-*C*), 29.69 (Alk-*C*), 29.73 (8 Alk-*C*), 31.95 (C_ρ), 68.25 C_ς), 107.44 (2 Ar-*C*), 121.34 (2 Ar-*C*), 123.73 (2 Ar-*C*), 136.73 (2 Ar-*C*), 149.02 (2 Ar-*C*), 156.27 (2 Ar-*C*), 157.04 (2 Ar-*C*), 167.4 (Ar-*C*) ppm. $C_{33}H_{47}N_3O$ (501.76): calcd. C 79.0, H 8.4, N 9.4; found C 78.7, H 8.4, N 9.5.

4′-(3-Chloropropoxy)-2,2′;6′,2″-terpyridine (12): (Hydroxypropoxy)terpyridine **11**[24] (3.00 g, 9.76 mmol) was carefully added to 10 mL of $SOCl_2$ (resulting in heat development!) and refluxed for 5 h. The remaining $SOCl_2$ was removed in vacuo and the residue was neutralized with saturated $NaHCO_3$ solution. The crude product was filtered off and dried in vacuo. The product was purified by recrystallization from ethanol to yield **12** as a colourless crystalline solid (2.10 g, 66%). M.p. 105 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.30 (m, 2 H, H_β), 3.78 (t, *J* = 6.3 Hz, 2 H, H_α), 4.39 (t, *J* = 5.8 Hz, 2 H, H_γ), 7.36 (ddd, *J* = 1.2, 4.8, 7.5 Hz, 2 H, $H_{5,5''}$), 7.85 (ddd, *J* = 1.8, 7.5, 7.5 Hz, 2 H, $H_{4,4''}$), 8.03 (s, 2 H, $H_{3',5'}$), 8.61 (ddd, *J* = 1.1, 2.1, 2.1 Hz, 2 H, $H_{3,3''}$), 8.69 (ddd, *J* = 0.9, 1.8, 4.8 Hz, 2 H, $H_{6,6''}$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 32.0 (C_β), 41.2 (C_α), 64.4 (C_γ), 107.3 ($C_{5,5''}$), 121.3 ($C_{4,4''}$), 123.8 ($C_{3,3''}$), 136.8 ($C_{3',5'}$), 149.0 ($C_{6,6''}$), 156.0 ($C_{2,2''}$), 157.1 ($C_{2',6'}$), 166.9 ($C_{4'}$) ppm. MALDI-TOF-MS (matrix: dithranol): *m*/*z* = 326 [MH^+]. EIMS (70 eV): *m*/*z* = 325 [M^+]. $C_{18}H_{16}ClN_3O$ (325.79): calcd. C 66.36, H 4.95, N 12.90; found C 66.0, H 5.0, N 13.0.

4′-[(1,2-Diphenylvinyl)oxy]-2,2′:6′,2″-terpyridine (13): Hydrobenzoin (202 mg, 0.943 mmol) was added to a stirred suspension of powdered KOH (224 mg, 3.99 mmol) in DMSO (30 mL) at 40 °C. After 20 min, 4′-chloro-2,2′:6′,2″-terpyridine (**1**, 505 mg, 1.89 mmol) was added. The mixture was stirred at 40 °C for 4 h and then poured into deionized water (300 mL). The aqueous phase was removed by filtration, and the product was washed with deionized water and dried in vacuo. The crude product was dissolved in ethyl acetate and an insoluble by-product was filtered off. Recrystallization from ethyl acetate yielded colourless crystals of **13** (96 mg, 15%). M.p. 192 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.82 (s, 1 H, =C*H*), 7.18 (ddd, *J* = 1.1, 1.1, 7.4 Hz, H_{aryl}), 7.31 (m, 3 H, H_{aryl}, 2 H, $H_{5,5''}$), 7.67 (m, 4 H, H_{aryl}), 7.81 (ddd, *J* = 1.8, 7.8, 7.8 Hz, 2 H, $H_{4,4''}$), 8.14 (s, 2 H, $H_{3',5'}$), 8.57 (ddd, *J* = 1.0, 1.0, 8.0 Hz, 2 H, $H_{3,3''}$), 8.65 (ddd, *J* = 0.8, 1.7, 4.7 Hz, 2 H, $H_{6,6''}$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 107.4 ($C_{5,5''}$), 113.5, 117.4 ($C_{stilbene}$), 121.3 ($C_{4,4''}$), 123.8 ($C_{3,3''}$), 125.8, 127.6, 128.6, 128.7, 129.2, 134.2, 135.2 ($C_{stilbene}$), 136.8 ($C_{3',5'}$), 144.1, 148.5 ($C_{stilbene}$), 149.0 ($C_{6,6''}$), 155.8 ($C_{2,2''}$), 157.5 ($C_{2',6'}$), 165.2 ($C_{4'}$) ppm. MALDI-TOF-MS (matrix: dithranol): *m*/*z* = 427 [M^+]. EIMS (70 eV): *m*/*z* = 427 [M^+]. UV/Vis ($CHCl_3$/MeOH 1:1): λ (ε) = 285 (13100), 320 (6001) nm. $C_{20}H_{22}N_4O$ (427.50): calcd. C 81.48, H 4.95, N 9.83; found C 81.71, H 4.83, N 9.82.

5-(1,2-Dithiolan-3-yl)-*N*-[5-(2,2′;6′,2″-terpyridin-4′-yloxy)pentyl]-pentanamide (14): (Aminopentoxy)terpyridine **2** (334 mg, 0.998 mmol), racemic thioctic acid (412 mg, 2.00 mmol), DCC (0.23 g, 1.1 mmol) and a catalytic amount of DMAP (ca. 4 mg) were stirred in dry $CHCl_3$ at room temp. for 10 h. After this time, the insoluble residue was filtered off and washed with 2 × 10 mL of dry $CHCl_3$. The filtrate was concentrated and the resulting crude residue was purified by column chromatography (Alox N, eluent: DCM, 0.5% MeOH). Further purification was carried out by recrystallization from diethyl ether (twice) to yield **14** as a light yellow solid (183 mg, 35%). R_f = 0.87 (alox N, CH_2Cl_2/MeOH, 99:1). M.p. 99 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.57 (m, 13 H), 1.89 (m, 2 H), 2.17 (t, *J* = 7.2 Hz, 2 H, NHCOCH_2), 2.43 (m, 1 H), 3.12 (m, 2 H), 3.30 (m, 2 H), 3.55 (m, 1 H), 4.23 (t, *J* = 6.2 Hz, 2 H, H_ε), 5.50 (s, 1 H, $CH_2NHCOCH_2$), 7.33 (ddd, *J* = 1.2, 4.8, 7.5 Hz, 2 H, $H_{5,5''}$), 7.85 (ddd, *J* = 1.8, 7.5, 7.5 Hz, 2 H, $H_{4,4''}$), 8.00 (s, 2 H, $H_{3',5'}$), 8.62 (d, *J* = 8.0 Hz, 2 H, $H_{3,3''}$), 8.69 (ddd, *J* = 1.0, 1.8, 4.8 Hz, 2 H, $H_{6,6''}$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 23.4, 25.4, 28.6, 28.8, 29.2, 34.5, 36.4, 38.4, 39.3, 40.1 (C_α, C_β, C_γ, C_δ, $CH_2NHCOCH_2CH_2$, CH_2CH_2CH, CH_2CH_2CH, CH_2CH_2CH, CH_2CHCH_2, $CH_2CHCH_2CH_2$), 56.4 (NHCOCH_2), 67.8 (C_ε) 107.3 ($C_{5,5''}$), 121.3 ($C_{4,4''}$), 123.8 ($C_{3,3''}$), 136.8 ($C_{3',5'}$), 148.9 ($C_{6,6''}$), 156.0 ($C_{2,2''}$), 157.0 ($C_{2',6'}$), 167.1 ($C_{4'}$), 172.6 ($NHCOCH_2$) ppm. MALDI-TOF-MS (matrix: dithranol): *m*/*z* = 523 [MH^+]. $C_{20}H_{22}N_4O$ (334.42): calcd. C 64.34, H 6.56, N 10.72; found C 64.2, H 6.6, N 10.8.

X-ray Crystallographic Data for Compounds 7 and 9: Data were collected with a Siemens P4 diffractometer, using Cu-K_α radiation (λ = 1.54178 Å) at 203 K. **7:** Crystal data: monoclinic, space group *C*2/*c*, *a* = 18.264 (2), *b* = 410.4469 (14), *c* = 16.966 (3) Å, *V* = 3237.3 (8) Å^3, *Z* = 2. Data collection: a crystal of ca. 0.25 × 0.15 × 0.15 mm was used to record 2048 reflections, $2\theta_{max}$ = 55.71°, completeness to θ = 55.87° was 94.9%. Structure refinement: the structure was refined anisotropically by full-matrix least squares on F^2 to *wR*2 = 0.1622, *R*1 = 0.0680. **9:** Crystal data: monoclinic, space group *C*2/*c*, *a* = 42.531 (9), *b* = 42.531 (9), *c* = 42.531 (9) Å, *V* = 4.72 (1) nm^3, *Z* = 2. Data collection: a crystal of ca. 0.75 × 0.05 × 0.03 mm was used to record 2793 reflections, $2\theta_{max}$ = 55.87°, completeness to θ = 55.87° was 90.4%. Structure refinement: the structure was refined anisotropically by full-matrix least-squares on F^2 to *wR*2 = 0.2283, *R*1 = 0.1066. CCDC-214912 (**7**) and -214913 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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