Alcohol- and water-soluble bis(tpy)quaterthiophenes with phosphonium side groups: new conjugated units for metallo-supramolecular polymers†

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Bis(tpy)quaterthiophenes with symmetrically distributed two and four 6-bromohexyl side groups were prepared and modified by the reaction with triethylphosphine to give the corresponding ionic species. Both ionic and non-ionic bis(tpy)quaterthiophenes (unimers) were assembled with Zn2+ and Fe2+ ions to conjugated metallo-supramolecular polymers (MSPs), of which the ionic ones are soluble in alcohols and those derived from tetrasubstituted unimers are soluble even in water. The differences in assembly are specified between systems with (i) ionic and non-ionic unimers, (ii) Zn2+ and Fe2+ ion couplers, and (iii) methanol and water solvents. A substantial decrease in the stability of Fe-MSPs and a surprisingly high red shift of the luminescence band of Zn-MSPs were observed on going from methanol to aqueous solutions.

Results and discussion

The prepared ionic as well as non-ionic unimers and their abbreviations are shown in Chart 1 together with the numbering of the central block positions and the marking of the rings used in the assignment of NMR spectra. The letter Q denotes...
the unimers with the quaterthiophene central block and the numbers behind it indicate the positions occupied by hexyl groups (suffix -H) or by hexyl groups capped with a 4-methoxyphenoxy group (suffix -A) or a bromine atom (suffix -Br) or a triethylphosphonium group (suffix -P+). The prefix PZn (polymers with Zn\(^{2+}\) ion couplers) or PFe (Fe\(^{2+}\) ion couplers) before the unimer label: for example, PZnQ27-Br denotes the MSPs formed by the assembly of Zn\(^{2+}\) ions and unimer Q27-Br that contains 6-bromohexyl groups attached to the quaterthiophene central block at positions 2 and 7; PFeQ45-P+ stands for the MSPs formed from Fe\(^{2+}\) ions and unimer Q45-P+ that contains two 6-(triethylphosphonium)hexyl groups attached to positions 4 and 5 of the central block, etc.

Synthesis and characterization of unimers and polymers

The reference unimers Q and Q27-H were prepared using the Suzuki–Miyaura coupling strategy (Scheme 1) and the conditions applied earlier.\(^{28,29,33}\) Br-unimers were prepared using the strategy shown in Schemes 1 and 2a. The starting monomer 3-[6-(4-methoxyphenoxy)hexyl]thiophene was prepared using the procedure described elsewhere.\(^ {34}\) The procedure starting from 3-(6-bromohexyl)thiophene used for the synthesis of ionic unimers with mono- (M) and bithiophene (B) central blocks\(^ {29}\) was not so effective owing to low efficiency of purification of unimers with bromohexyl groups. Connecting \(\text{tpy}\) end-groups by Suzuki coupling (Scheme 1c) was accompanied by partial dehydrobromination of bromohexyl side groups promoted with \(\text{tpy}\) end-groups.\(^ {29}\) Purification of short unimers could be done easily (for M) or feasibly (for B), but the purification of bis\(\text{tpy}\)quaterthiophenes was almost impossible.

The use of new starting monomers avoided the above difficulties and, in addition, made the isolation of all intermediates as well as A-unimers much easier. The A-unimers were then allowed to react with BB\(_3\) (Scheme 2a) to give the corresponding Br-unimers with bromohexyl side groups (yield 85–95\%), which were finally treated with triethylphosphine to give the corresponding ionic P+ unimers (Scheme 2b). Excess PEt\(_3\) was easily removed by vacuum distillation and its oxide (POET\(_3\)) was washed away with toluene and ether. Solid products were isolated by centrifugation (yield of the ionization step was from 75 to 95\%).

Solubility in methanol was the first evidence of successful transformation of the Br- into P+ unimers. The NMR spectra of modified unimers accordingly showed a \(^{31}\)P signal of P+ groups at around 39 ppm (38.93 for Q27-P+, 38.44 for Q45-P+, 39.99 for Q2457-P+). \(^1\)H signals of ethyl groups (part of P+) but no signal at 3.4 ppm that is typical of CH\(_2\)-Br groups. Weak \(^1\)H signals at 5.93 ppm and 5.55–5.45 ppm were also observed indicating that some side chains contain terminal double bonds formed by dehydrobromination accompanying quaternization of Br-unimers. Complete removal of imperfect molecules from P+ unimers was not successful since they are soluble in alcohols.

TGA analyses of Br-unimers and P+ unimers showed thermal stability up to 205 °C.

Metallo-supramolecular polymers were simply prepared by mixing solutions of a given unimer and zinc(II) or iron(II) perchlorate in the metal ions to a unimer mole ratio of \(r = 1\) (\(r = [\text{Mt}^{2+}] / [\text{unimer}]\)). Br-unimers were assembled in the acetonitrile/chloroform mixed solvent (1/1 by vol.) while P+ unimers were assembled in methanol.

The solubility of the prepared unimers and polymers depends on the substitution of the unimer central block. The unsubstituted unimer Q is soluble in dichloromethane but poorly soluble in chloroform. Br-unimers are highly soluble in solvents such as THF, CHCl\(_3\), CH\(_2\)Cl\(_2\), DMSO and the acetonitrile/chloroform mixture, which facilitates their isolation and purification. Unimers with two ionic groups are highly
soluble in polar solvents such as methanol, ethanol and DMSO and sparingly soluble in water (complete dissolution to a colloidal solution takes a few weeks). Unimer Q2457-P⁺ carrying four ionic groups is easily soluble in water, which is quite unusual for this type of conjugated structure. Nevertheless, complete dissolution of Q2457-P⁺ to the molecular level takes time on the day scale as can be seen from the time development of the UV/vis spectrum of its aqueous solution shown in Fig. S1, ESI.† MSPs show similar solubility to the corresponding unimers.

**Vibrational spectra of unimers and polymers**
The IR spectra of unimers show each the bands of stretching modes \((\nu_{CC}, \nu_{CN})\) of tpy end-groups (1500–1620 \(\text{cm}^{-1}\)), the
The band at 1472 cm\(^{-1}\) whose intensities depend on the positions of side groups. The band is composed of at least five bands (Fig. S4b). The OMNIC software gave robust results, showing that this band is overlapped by the ring stretching modes of the quaterthiophene central blocks. Only a small shift of the band maximum from 1459 cm\(^{-1}\) (for Q) to 1466 cm\(^{-1}\) (for Q27-H) and a new shoulder at 1384 cm\(^{-1}\) for Q27-H are observable. The broad spectral band at 3400 cm\(^{-1}\) observed for all P\(^{+}\)-unimers is due to the presence of hydrogen bonded water molecules in these unimers.

The off-resonance Raman spectra of unimers show strong stretching bands of quaterthiophene blocks but weak bands of tpy end-groups. Their spectral patterns reflect differences in the substitution of quaterthiophene blocks (Fig. S3, ESI†). The Raman spectra of Zn-polymers were distorted by strong fluorescence but spectra of non-fluorescent Fe-polymers were well measurable. The bands characteristic of tpy groups occur at 1610 cm\(^{-1}\) (\(\nu_s\)), 1290 cm\(^{-1}\) (\(\delta_{HH}\)) and 1038 cm\(^{-1}\) (breathing mode) while the bands of quaterthiophene blocks occur in the region 1380–1520 cm\(^{-1}\) (Fig. S4a–S7a, ESI†). Deconvolution of the latter band using the OMNIC software gave robust results, showing that this band is composed of at least five bands (Fig. S4b–S7b, ESI†) whose intensities depend on the positions of side groups. The band at 1472 cm\(^{-1}\) should also be attributed to transitions in tpy groups.

**Optical spectra of unimers and polymers**

The solution UV/vis absorption spectra of unimers (ESI, Fig. S8a†) show: (i) a flat band at 280–284 nm mainly contributed by transitions in tpy end-groups, and (ii) a band with the apex at a wavelength \(\lambda_A\) from 381 nm (Q2457-P\(^{+}\)) to 441 nm (Q) belonging to transitions from HOMO that is spread over thiophene rings and central rings of tpy groups. The value of \(\lambda_A\) (see Table 1) decreases (i) with increasing distortion of the quaterthiophene central block (see Table 2), and (ii) on going from the non-ionic (-Br, -H) to ionic unimer (-P\(^{+}\)) of the same type. Absorption maxima in the spectra of unimer thin films (ESI, Fig. S8b†) are not in such good correlation with the chain distortion, which reflects the importance of the molecular packing effect or the electronic effect of substituents. An exceptionally high \(\lambda_A\) of Q2457-Br thin films (500 ± 10 nm) was obtained. The fact that Q2457-P\(^{+}\) shows much lower \(\lambda_A\) can be ascribed to the bulkiness of P’Et\(_3\) groups and the effect of bromine counterions.

In the spectra of Zn-polymers, the absorption band of transitions involving quaterthiophene blocks is red shifted by about 35–65 nm compared to its position \(\lambda_A\) for the unimer in the solution spectra and by about 20–75 nm in thin films (Table 1). The only but great exception is the spectrum of P\(_{20}\)Q2457-Br thin films that surprisingly shows a blue shift of \(\lambda_A\) of about –70 nm, which is obviously due to the exceptionally high value of \(\lambda_A\) of the unimer Q2457-Br.

The spectra of Fe-polymers contain a new band belonging to transitions in the metal-to-ligand charge transfer (MLCT) complex which is typical of tpy-Fe-tpy linkages (ESI†) (see Table 1 and Fig. S8c and S8d in the ESI†). In Fe-polymers, this band is significantly contributed by transitions involving neighboring oligothiophene blocks.
Luminescence spectra of unimers in solutions (ESI, Fig. S9a†) show higher similarity than their UV/vis spectra (λF around 550 nm; lowered values of about 535 nm are actually given by different band shapes). This is obviously due to the fast transition of excited unimer molecules to nearly coplanar conformations with quinoidal rings, from which the light emission takes place.36 Minor differences are nevertheless seen: unimers with less distorted chains (Q, Q27-H, Q27-Br and Q27-P†) show a better resolved vibrational structure than unimers with more distorted chains (Q45-Br, Q45-P+, Q2457-Br and Q2457-P†). The luminescence spectra of unimers and Zn-polymer thin films are shown in ESI, Fig. S9b–d† and the band wavelengths are summarized in Table 1, and the luminescence lifetimes are presented in ESI, Table S1.† Fe-polymers do not show luminescence.28,29,36

Table 1  UV/vis and luminescence spectral characteristics of the prepared unimers and polymers; solvent: methanol for ionic unimers and polymers (suffix -P†); acetonitrile/chloroform (1/1 by vol.) for all the other unimers and polymers. λA – apex of absorbance maxima; λF – apex of emission maxima; ν – Stokes shift; λMLCT – apex of the MLCT band; Φ – absolute luminescence quantum yield

<table>
<thead>
<tr>
<th>Sample</th>
<th>UV/vis absorption</th>
<th>Luminescence</th>
<th>Stokes shift</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λA, nm</td>
<td>λF, nm (Φ, %)</td>
<td>ν, cm⁻¹</td>
</tr>
<tr>
<td></td>
<td>Solution</td>
<td>Film</td>
<td>Solution</td>
</tr>
<tr>
<td>Q</td>
<td>441</td>
<td>456 (30%)</td>
<td>~645 (&lt;1%)</td>
</tr>
<tr>
<td>Q27-H</td>
<td>425</td>
<td>456 (30%)</td>
<td>~630 (1%)</td>
</tr>
<tr>
<td>Q27-Br</td>
<td>425</td>
<td>455 (31%)</td>
<td>~630 (1%)</td>
</tr>
<tr>
<td>Q27-P†</td>
<td>419</td>
<td>455 (18%)</td>
<td>~650 (&lt;1%)</td>
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<tr>
<td>Q45-Br</td>
<td>397</td>
<td>425 (14%)</td>
<td>610 (1%)</td>
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<tr>
<td>Q45-P†</td>
<td>393</td>
<td>410 (11%)</td>
<td>550 (1%)</td>
</tr>
<tr>
<td>Q2457-Br</td>
<td>386</td>
<td>500 (14%)</td>
<td>560, 603 (3%)</td>
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<td>Q2457-P†</td>
<td>381</td>
<td>410 (10%)</td>
<td>560 (1%)</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>555</td>
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Zn polymers

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<tr>
<th>Sample</th>
<th>UV/vis absorption</th>
<th>Luminescence</th>
<th>Stokes shift</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λA, nm (λMLCT, nm)</td>
<td>ν, cm⁻¹</td>
<td>Solution</td>
</tr>
<tr>
<td>PZnQ</td>
<td>486 (500)</td>
<td>~650 (&lt;1%)</td>
<td>5350</td>
</tr>
<tr>
<td>PZnQ27-H</td>
<td>468 (490)</td>
<td>~640 (2%)</td>
<td>6500</td>
</tr>
<tr>
<td>PZnQ27-Br</td>
<td>470 (510)</td>
<td>~710 (1%)</td>
<td>6450</td>
</tr>
<tr>
<td>PZnQ27-P†</td>
<td>483 (500)</td>
<td>~703 (&lt;1%)</td>
<td>2500</td>
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<tr>
<td>PZnQ45-Br</td>
<td>447 (455)</td>
<td>585 (3%)</td>
<td>7500</td>
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<tr>
<td>PZnQ45-P†</td>
<td>426 (430)</td>
<td>660 (1%)</td>
<td>4800</td>
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<tr>
<td>PZnQ2457-Br</td>
<td>432 (430)</td>
<td>590 (3%)</td>
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<tr>
<td>PZnQ2457-P†</td>
<td>439 (440)</td>
<td>625 (1%)</td>
<td>4650</td>
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<td></td>
<td>462*</td>
<td>720*</td>
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Fe polymers

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<th>Luminescence</th>
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<tbody>
<tr>
<td></td>
<td>λA, nm (λMLCT, nm)</td>
<td>Solution</td>
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<tr>
<td>PFeQ</td>
<td>395, 471 (603)</td>
<td>475 (621)</td>
</tr>
<tr>
<td>PFeQ27-H</td>
<td>437 (601)</td>
<td>460 (622)</td>
</tr>
<tr>
<td>PFeQ27-Br</td>
<td>387, 452 (601)</td>
<td>465 (621)</td>
</tr>
<tr>
<td>PFeQ27-P†</td>
<td>386, 436 (593)</td>
<td>465 (611)</td>
</tr>
<tr>
<td>PFeQ45-Br</td>
<td>405 (598)</td>
<td>410 (613)</td>
</tr>
<tr>
<td>PFeQ45-P†</td>
<td>399 (593)</td>
<td>410 (609)</td>
</tr>
<tr>
<td>PFeQ2457-Br</td>
<td>384, 423s (594)</td>
<td>395* (609)</td>
</tr>
<tr>
<td>PFeQ2457-P†</td>
<td>384 (591)</td>
<td>395* (604)</td>
</tr>
<tr>
<td>PFeQ2457-P†</td>
<td>400 (607)*</td>
<td></td>
</tr>
</tbody>
</table>

* Data from aqueous solution.  b Shoulders.

Table 2  Calculated geometry of the unimers; δBC⋯δDD are dihedral angles between the planes of neighbouring main-chain rings given in subscript (for ring labels see Chart 1)

<table>
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<th>Sample</th>
<th>Ground state</th>
<th>Excited state</th>
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<tr>
<td></td>
<td>δBC</td>
<td>δCD</td>
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<tr>
<td>Q</td>
<td>15.8</td>
<td>12.3</td>
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<tr>
<td>Q27-H</td>
<td>17.3</td>
<td>28.6</td>
</tr>
<tr>
<td>Q27-Br</td>
<td>13.9</td>
<td>22.8</td>
</tr>
<tr>
<td>Q27-Br-</td>
<td>17.3</td>
<td>32.4</td>
</tr>
<tr>
<td>Q45-Br</td>
<td>14.6</td>
<td>18.5</td>
</tr>
<tr>
<td>Q45-Br-</td>
<td>18.0</td>
<td>15.4</td>
</tr>
<tr>
<td>Q2457-Br</td>
<td>19.6</td>
<td>40.8</td>
</tr>
<tr>
<td>Q2457-Br-</td>
<td>15.8</td>
<td>27.4</td>
</tr>
</tbody>
</table>

* Values are not available for the first 720 hours.
Assembly of unimers to metallo-supramolecular polymers in solutions

The assembly in solutions was monitored by UV/vis and luminescence spectroscopy, viscometry and size exclusion chromatography (SEC). A chloroform/acetonitrile mixed solvent (1/1 by volume) was used for Br-unimers while methanol and water were used for P-unimers. For spectroscopic studies, a set of solutions of a constant unimer concentration (2 × 10^{-5} M) and a stepwise increasing metal ions to unimer mole ratio (r from 0 to 3) was prepared for each Mt^{2+}/unimer system and solutions were allowed to equilibrate for 24 hours before monitoring the spectra. The SEC and viscometric measurements were done with solutions of the concentration of 5 × 10^{-4} M.

Spectral changes accompanying the assembly of unimers with Mt^{2+} ions showed three stages differing in the development trend, similarly to the related systems studied recently.^{21,25,28,29,40} The UV/vis spectra obtained for systems of composition ratios r from 0 to ca. 0.5 (the first stage of assembly) showed up to three isosbestic points (see examples in Fig. 1a and 2a and a complete set of the spectra in ESI, Fig. S10 and S11†), which indicates the transformation of the unimer species into another well-defined species. Regarding the stoichiometry, the new species should be a dimer species unimer-Mt^{2+}-unimer.

The spectra obtained for systems with ratios r from ca. 0.6 to 1 also show isosbestic points but at different wavelengths (Fig. 1b and 2b). This indicates that the systems entered the second stage of assembly in which longer polymer chains are formed. As can be seen from ESI, Fig. S10 and S11† the absorption bands characteristic of free unimers and dimers disappear while the band of enchainned unimer units fully develops in the case of systems with non-ionic Br-unimers. These systems then enter the third stage of assembly (r > 1), where spectral changes are quite low and can be attributed to the end-capping of polymer chains with the metal ions and partial depolymerization of the polymer chains to the shorter

Fig. 1 Changes in UV/vis spectra accompanying the titration of ionic unimers with Zn^{2+} ions. Initial unimer concentration 2 × 10^{-5} M in methanol, room temperature. Column (a) shows the first stage of assembly, column (b) shows the second stage and column (c) shows the third stage; see the text.

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also end-capped ones (Fig. 1c and 2c). The reaction of (tpy)$_2$Zn$^{2+}$ species with Zn$^{2+}$ ions giving two (tpy)Zn$^{2+}$ species has been reported for mono- as well as bis(tpy) species. The reaction of (tpy)$_2$Fe$^{2+}$ species with Fe$^{2+}$ ions giving two (tpy)Fe$^{2+}$ species was reported only for metallo-supramolecular polymers. The spectral changes in the second stage of assembly of ionic P$^+$-unimers are less progressive than those in the case of Br-unimers or even incomplete, which indicates lowered thermodynamic stability (i.e., stability constants) of ionic polymers in methanol. The lowered stability of ionic Fe-polymers is also seen from the changes in the position and intensity of the MLCT band (at around 595 nm) that is not fully developed at the ratio $r \approx 1$ (Fig. 2b). The UV/vis spectral patterns indicate that the ionic polymers acquire their maximum length at the ratios $r$ of about 1.5 or higher in methanol solutions.

The changes in luminescence spectra accompanying the assembly of ionic unimers with Zn$^{2+}$ ions are shown in Fig. 3. The complexation is manifested by the disappearance of the unimer emission band and the creation of a new band red shifted by about 130 nm. Unlike the case of shorter ionic polymers derived from bis(tpy) mono- and bithiophenes, the new emission band is much less intense than the band of free unimers. A similar luminescence attenuation is also exhibited by systems with non-ionic polymers. This shows that the prolongation of the unimer central oligothiophene block increases the efficiency of non-radiative paths of the decay of excited states in Zn-polymers.

Unlike the systems with Zn$^{2+}$ ions, those with Fe$^{2+}$ ions show a monotonous luminescence quenching with increasing ratios $r$ up to ca. 0.6, at which the luminescence disappears (for example see ESI, Fig. S12†). This behaviour, which is exhibited by other systems with bis(tpy)Fe$^{2+}$ species, is attributed to the fact that the lowest excited state of bis(tpy)Fe$^{2+}$ species, the d–d triplet state, is close to the ground state. As the d–d triplet state easily depletes higher excited states and potential phosphorescence from the d–d state is spin forbid-

![Fig. 2](Changes in UV/vis spectra accompanying the titration of ionic unimers with Fe$^{2+}$ ions. Initial unimer concentration $2 \times 10^{-5}$ M in methanol, room temperature. Column (a) shows the first stage of assembly, column (b) shows the second stage and column (c) shows the third stage; see the text.)
den, its decay by non-radiative transitions is unambiguously preferred in accord with the energy gap law.\textsuperscript{8,45}

The molar mass distribution of Br-polymers in CHCl\textsubscript{3}/CH\textsubscript{3}CN (1:1) solutions was examined using an SEC system equipped with a diode-array UV/vis detector (DAD). (Analysis of ionic polymers failed owing to the strong adsorption of their chains inside SEC columns.) Mixed solutions of a Br-unimer (0.5 mM) and Zn\textsuperscript{2+} or Fe\textsuperscript{2+} ions (r from 0 to 2.0) equilibrated for one day were injected into the SEC system. The SEC records of systems with Zn\textsuperscript{2+} ions showed nothing but the peak of free unimers, which proves rapid dissociation of the Zn-polymer chains upon multifold dilution of their solution inside SEC columns. In contrast, the systems with Fe\textsuperscript{2+} ions provided SEC records typical of covalent polymers (Fig. 4 and ESI, S13†), which demonstrates very slow constitutional dynamics of Fe-polymers in the used solvent. Similar results were recently obtained for MSPs of shorter bis(py)thiophenes.\textsuperscript{29}

Well resolved SEC records were obtained only for systems with a composition ratio r < 1 (Fig. 4). Systems with r \geq 1 gave poorly resolved SEC records, in which the area under the elution peak decreased with increasing value of r. This indicates retention of longer chains in SEC columns. The detached polymer chains, obviously end-capped with Fe\textsuperscript{2+} ions, had to be additionally washed out of the columns with 2,2′-bipyridine. The UV/vis spectral pattern of SEC fractions showed a perfect development with the elution time (t\textsubscript{el}); a pattern typical of long polymer chains was observed for the first eluted SEC fractions while that typical of the dimers for the last fraction (Fig. 5a and ESI, Fig. S14a†). Differences are also seen when comparing the spectra of fractions of dimers formed in systems of different compositions (Fig. 5b and ESI, Fig. S14b†). These differences can be attributed to the end-capping of their molecules with Fe\textsuperscript{2+} ions. However, these differences are substantially smaller than those observed for the Fe-polymers formed from unimers with mono- and bithiophene central blocks.\textsuperscript{29}

The presence of higher fractions in solutions containing a stoichiometric lack of Fe\textsuperscript{2+} ions (r = 0.2 and 0.5) can be explained by the transiently locally increased concentration of the ions and unimers during mixing of their solutions. The formation of polymer chains is most likely a kinetically con-

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**Fig. 3** Changes in photoluminescence spectra accompanying the titration of ionic unimers with Zn\textsuperscript{2+} ions. Initial unimer concentration 2 x 10^{-5} M in methanol, room temperature.

**Fig. 4** The SEC records of the Fe\textsuperscript{2+}/Q45-Br systems of different compositions.
The water-soluble unimer \( Q2457-P^+ \) has been assembled with metal ions also in aqueous solutions. Since molecular dissolution of this unimer in water takes a long time a month-old solution of \( Q2457-P^+ \) was used in these experiments. As can be seen from Fig. 6, the optical spectral changes accompanying the assembly in water substantially differ from those observed for assembly in methanol.

(i) The absorption maxima of \( Q2457-P^+ \) (\( \lambda_A = 400 \) nm) and its Zn-polymer (\( r = 2, \lambda_A = 462 \) nm) as well as the luminescence maximum of the unimer (\( \lambda_F = 555 \) nm) are red shifted by about ca. 20 nm compared to their positions in methanol solutions, which indicates that the free as well as enchained unimer species acquire more planar conformations in water than in methanol. This can be attributed to the substantial increase in the solvent permittivity, which, in accord with the Coulomb law, reduces repulsive ionic interactions among neighbouring \( P^+Et_3 \) groups as well as their attractive interactions with counterions.

(ii) The luminescence emission band observed for Zn-polymer (\( \lambda_L = 720 \) nm) is enormously red shifted (about 168 nm) compared to the band for methanol solution. The Stokes shift for \( P_{Zn}Q2457-P^+ \) in water (7750 cm\(^{-1}\)) is much higher than the shift in methanol (4650 cm\(^{-1}\), Table 1), which proves the much higher extent of conformational relaxation of excited states in aqueous compared to methanol solutions.

(iii) The UV/vis spectra for assembly of \( Q2457-P^+ \) with Zn\(^{2+} \) ions show a single set of isosbestic points and a fluent course of changes up to \( r = 2 \). Luminescence spectra indicate the presence of free unimers in solution with \( r \) equal to at least 1.5. These features consistently indicate a lowered stability and increased constitutions dynamics of \( P_{Zn}Q2457-P^+ \) in aqueous solutions.

(iv) Surprisingly, in accord with the last mentioned observations, the UV/vis spectra for assembly of \( Q2457-P^+ \) with Fe\(^{2+} \) ions show small changes and a weak MLCT band and the luminescence spectra show emission even at the composition ratio \( r = 3 \). It should be stressed here that no new emission band occurs; only reluctant luminescence quenching with increasing \( r \) is observed. The observed spectral changes indicate that the chains of a highly ionic Fe-polymer are, in aqueous solution, less stable than the chains of its Zn-counterpart. This observation represents a flip in the stability of
Fe- and Zn-polymers derived from bis(tpy)quaterthiophenes compared to perhaps all the data reported so far.\textsuperscript{41,46–49} The reduced stability of the ionic Fe-polymer in water is obviously associated with the inhibition of the MLCT process by water. The solvent dependence of the MLCT is well known.\textsuperscript{50,51}

Conclusions

The synthesis strategy developed here enables preparation of bis(tpy)quaterthiophenes with two or four side groups symmetrically distributed along the quaterthiophene central block. The modification of side groups enabled preparation of ionic unimers that are soluble in green solvents such as alcohols or even in water.

Optical spectral patterns of dissolved unimers and the corresponding polymers depend primarily on the distribution of side groups along the quaterthiophene central block and only secondarily on the nature of side-chain-capping groups. The effect of the latter is more apparent in the solid state spectra since the capping groups significantly influence molecular packing.

During the assembly of unimers with metal ions the development of UV/vis spectra with increasing ratio \( r \) conclusively indicates that the \( \text{P}^{+} \)-unimers assemble with metal ions less readily than the \( \text{Br} \)-unimers. Besides, in water, \( \text{QZnQ}^{2+} \) assembles with \( \text{Zn}^{2+} \) ions considerably less progressively (with rising \( r \)) than in methanol and, with \( \text{Fe}^{2+} \) ions, still much less readily, showing only a very weak MLCT band but significant luminescence of the free unimer even at the ratio \( r = 3 \). The solvation effect is thus obvious. A red shift of the luminescence band of \( \text{PZnQ}^{2+} \) by about ca. 170 nm on going from methanol to aqueous solution is observed. Such a big shift indicates much higher conformational freedom of \( \text{PZnQ}^{2+} \) chains in aqueous compared to methanol solutions.

The SEC study of the non-ionic polymers proved that the constitutional dynamics of Zn-polymers is fast and that of Fe-polymers is very slow in the chloroform/acetonitrile mixed solvent, which is in accord with observations of other authors.

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**Fig. 6** Changes in UV/vis (left column) and photoluminescence (right column) spectra accompanying the titration of ionic unimers with \( \text{Zn}^{2+} \) or \( \text{Fe}^{2+} \) ions. Initial unimer concentration \( 2 \times 10^{-5} \) M in water, room temperature.
on related systems. However, the results obtained here on assembly of the ionic unimers in aqueous solutions anticipate faster constitutional dynamics of Fe-polymers compared to Zn-polymers.

**Experimental section**

**Materials**

2,2'-Bithiophene-5-boronic acid pinacol ester, 2,2'-bithiophene-5,5'-diboronic acid bis(pinacol) ester, thiopeine-2-boronic acid pinacol ester, 3,3’-diethyl-2,2’:5’:2’”-quaterthiophene, bis(pinacolato)diaboron (B₂pin), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin), 4,4’-di-tert-butyl-2,2’-dipyridyl (dbpy), bis(1,5-cyclooctadiene)di-μ-methoxydiiridium(i) ([Ir(OMe)(COD)]₂), boron tribromide (BBr₃), triethylphosphine (PE₃), 1.0 M in THF), N-bromosuccinimide (NBS), [1,3-bis(2,6-diisopropynylphenyl)imidazol-2-ylidene][3-chloropropyridyl]palladium(ii) dichloride (PEPPSI-IPr), zinc perchlorate hexahydrate, iron(II) phosphate (all Aldrich), K₂CO₃, MgSO₄, acetic acid (Lachner) and diethylether, dichloromethane, chloroform (Lachner) were used as obtained.

Before use, methanol (Aldrich) was bubbled with argon before use, and diethylether, dichloromethane, chloroform (Lachner) was distilled from LiAlH₄ before use, hexane (Lachner) was stored over a molecular sieve, tetrahydrofuran (Aldrich) was distilled from LiAlH₄ before use, and acetonitrile (ACN) were used as obtained.

**Measurements**

³¹H and ¹³C NMR spectra were recorded on a Varian UNITYINOVA 400 or a Varian SYSTEM 300 instrument in d₄-THF, d₅-CDCl₃, d₆-DMso or d₆-CDOD and referenced to the solvent signal: 7.25 ppm (d₆-CDCl₃), 5.32 ppm (d₅-CDCl₃), 3.58 ppm (d₅-THF), 2.50 ppm (d₆-DMso) or 3.31 ppm (d₆-CDOD) for ³¹H and 77.0 ppm (d₆-CDCl₃), 53.84 ppm (d₅-CDCl₃), 67.57 ppm (d₅-THF) or 49.15 ppm (d₆-CDOD) for ¹³C spectra. Coupling constants, J (in Hz), were obtained by the first-order analysis. Infrared spectra were recorded on a Thermo Nicolet 7600 FTIR spectrometer equipped with a Spectra Tech InspectIR Plus microscopic accessory using KBr-diluted samples and the diffuse reflectance technique (DRIFT) (128 or more scans at a resolution of 4 cm⁻¹). Raman spectra of solid samples were recorded on a DXR Raman microscope (Thermo Scientific) using excitations across the whole visible region (λₑₓ = 445, 532, 633 and 780 nm) and the usual laser power at the sample 0.1–0.4 mW. UV/vis spectra were recorded on a Shimadzu UV-2401PC instrument or a SPECORDER instrument in methanol or CHCl₃/ACN (1/1, v/v); solid samples were coated on the surface of a quartz cuvette. Photoluminescence spectra were recorded on a Fluorolog 3-22 Jobin Yvon SpeX instrument, using a four-window quartz cuvette (1 cm) for solutions and using quartz glass for films. The emission spectra were recorded with the excitation wavelength, λₑₓ, matching the absorption maximum of the measured sample. Quantum yields, Φₛ, of photoluminescence were measured using the integration sphere Quanta-F 3029. Fluorescence decay was monitored with a FluorHub single photon counting controller on a Fluorolog 3-22 Jobin Yvon SpeX instrument using excitation at λₑₓ = 378 nm for solutions and λₑₓ = 472 nm for films. Viscometric measurements were performed on a Microviscometer Lovis 2000 M/Me (Anton Paar). SEC recordings were obtained using a Spectra Physics Analytical HPLC pump P1000 with two SEC columns: Polymer Labs (Bristol, USA) Mixed-D and Mixed-E. The system was equipped with a Thermo UV6000 DAD detector. 0.05 M tetrabutylammonium hexafluorophosphate in CHCl₃/ACN (1/1, v/v, CHROMASOLV, Riedel-deHaen) was used as an eluent (0.7 mL min⁻¹).

5-(2,2′:6′,2′″-Terpyridine-4′-y1)-2,2′-bithiophene. 2,2′-Bithiophene-5-boronic acid pinacol ester (0.509 g, 1.74 mmol), Brₚpy (0.439 g, 1.41 mmol), K₂CO₃ (0.59 g, 4.26 mmol) and PEPPSI-IPr (50 mg) were placed in a Schlenk tube. Vacuum-argon cycles were applied several times and toluene (10 mL) and methanol (10 mL) were added through the septum. The reaction mixture was heated at 90 °C overnight. After cooling to room temperature the reaction mixture was diluted with dichloromethane (50 mL) and washed with water (3 × 200 mL). The organic layer was dried with MgSO₄, filtered and evaporated to obtain the crude product. The crude product was contaminated with bithiophene, which was washed off with hexane to obtain the pure product as a yellow powder (0.53 g, 95%). ¹H NMR (400 MHz, d₅-CDCl₃) δ ppm 8.74–8.72 (m, 2H, A³), 8.70 (s, 2H, B³), 8.67 (m, 2H, A²), 7.90 (td, 2H, J₁ = 7.7, J₂ = 1.7, A⁴), 7.73–7.71 (m, 1H, C⁴), 7.40–7.37 (m, 2H, A⁵), 7.33–7.31 (m, 2H, C⁳ + C⁵), 7.29 (d, J = 3.8, 1H, D²), 7.10–7.08 (m, 1H, D³). ¹³C NMR (101 MHz, d₅-CDCl₃) δ ppm 156.49, 156.10, 149.48, 143.11, 141.15, 140.61, 139.30, 128.39, 126.89, 125.53, 125.10, 124.69, 124.32, 121.36, 116.71. IR (DRIFT), cm⁻¹: 3086 (m), 3066 (m), 3013 (m), 2988 (w), 2965 (w), 2922 (m), 2871 (w), 2856 (w), 1598 (s), 1598 (s), 1565 (s), 1533 (m), 1541 (m), 1509 (m), 1464 (s), 1435 (m), 1422 (m), 1399 (s), 1366 (w), 1353 (w), 1323 (w), 1306 (w), 1290 (w), 1267 (m), 1253 (w), 1239 (m), 1232 (m), 1227 (m), 1209 (w), 1184 (w), 1162 (w), 1146 (w), 1124 (m), 1092 (m), 1077 (w), 1064 (m), 1051 (m), 1044 (m), 1010 (m), 988 (m), 961 (w), 954 (w), 915 (w), 898 (w), 885 (m), 878 (m), 838 (m), 789 (s), 773 (m), 746 (m), 741 (m), 730 (m), 717 (s), 690 (m), 683 (m), 668 (m), 658 (m), 643 (m), 632 (m), 622 (m), 587 (w), 565 (w), 523 (m), 489 (m), 466 (m), 447 (w), 418 (w), 402 (m). HRMS found m/z: 420.05998 [M⁺Na⁺], C₂₃H₁₄N₃NaS₂ requires: 420.05996.

5-Bromo-5-(2,2′:6′,2′″-Terpyridine-4′-y1)-2,2′-bithiophene. 5-(2,2′:6′,2′′-Terpyridine-4′-y1)-2,2′-bithiophene (0.52 g, 1.31 mmol) was dissolved in dichloromethane (20 mL) and acetic acid (20 mL), and NBS (0.26 g, 1.46 mmol) was added in the dark and the reaction mixture was stirred overnight. Then the acidic mixture was slightly neutralized by using a saturated solution of K₂CO₃ in water, diluted with dichloromethane (40 mL) and washed with water (3 × 250 mL). The organic layer was dried with MgSO₄, filtered and evaporated to obtain the product as a yellow solid (0.52 g, 83%). ¹H NMR (400 MHz, d₅-CDCl₃) δ ppm 8.74–8.72 (m, 2H, A³), 8.68–8.65 (m, 4H, A³ + B³), 7.90 (td, J₁ = 7.8, J₂ = 1.8, 2H, A²), 7.71 (d, J = 3.8, 1H, C⁴), 7.38
product precipitated. The suspension was filtered, washed with MgSO₄, filtered and evaporated to obtain the product as a

\[ \text{[M+H]}⁺, \text{C}_{58}\text{H}_{33}\text{N}_6\text{S}_4 \text{ requires: } 961.3209 \]  

IR (DRIFT), \( \text{cm}⁻¹ \) 3064 (m), 3012 (m), 2991 (w), 2937 (w), 1718 (w), 1599 (s), 1582 (s), 1567 (s), 1551 (s), 1508 (w), 1476 (m), 1466 (m), 1459 (m), 1438 (m), 1400 (m), 1365 (w), 1327 (w), 1308 (w), 1292 (w), 1266 (w), 1251 (w), 1237 (w), 1208 (w), 1126 (m), 1094 (m), 1079 (w), 1042 (m), 1011 (m), 988 (m), 963 (w), 919 (w), 898 (w), 872 (m), 855 (m), 849 (w), 786 (s), 742 (s), 732 (m), 726 (m), 690 (m), 683 (m), 667 (m), 660 (m), 640 (m), 633 (m), 621 (m), 564 (m), 518 (w), 485 (m), 466 (m), 408 (m). HRMS found \( m/z \): 793.13281 [M⁺H]⁺; \( \text{C}_{49}\text{H}_{23}\text{N}_4\text{S}_4 \) requires: 793.13310.

3,3′′-Dihexyl-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1) Q. 5-Bromo-5′-2,2′:5′:2′′-terpyridine-4-y1)-2,2-bithiophene (0.372 g, 0.78 mmol), B_bpin (0.168 g, 0.66 mmol), K₂CO₃ (0.34 g, 2.46 mmol) and PEPPSI-Ipr (25 mg) were placed in a Schlenk tube and vacuum–argon cycles were applied. 

Then toluene (15 mL) and methanol (15 mL) were added through the septum and the reaction mixture was heated at 90 °C overnight. After cooling to room temperature the mixture was diluted with dichloromethane (30 mL) and washed with water (3 x 200 mL). The organic layer was dried with MgSO₄, filtered and evaporated to obtain the crude product. The product was purified by column chromatography (Al₂O₃, hexane/THF, 3:2).

Orange powder (0.12 g, 17%). 1H NMR (400 MHz, d₅-CDCl₃) \( \delta \) ppm 8.78–8.76 (m, 4H, A⁴), 8.64 (s, 4H, B⁴), 8.66 (s, 4H, A⁵), 7.98 (s, 2H, C⁵), 7.32–7.21 (m, 4H, D⁴ + D⁵). The low solubility of this compound we were not able to obtain the ¹³C NMR spectrum in a sufficient quality. IR (DRIFT), \( \text{cm}⁻¹ \) 3063 (m), 3012 (w), 2991 (w), 2937 (w), 1718 (w), 1599 (s), 1582 (s), 1567 (s), 1551 (s), 1508 (w), 1476 (m), 1466 (m), 1459 (m), 1438 (m), 1400 (m), 1365 (w), 1327 (w), 1308 (w), 1292 (w), 1266 (w), 1251 (w), 1237 (w), 1208 (w), 1126 (m), 1094 (m), 1079 (w), 1042 (m), 1011 (m), 988 (m), 963 (w), 919 (w), 898 (w), 872 (m), 855 (m), 849 (w), 786 (s), 742 (s), 732 (m), 726 (m), 690 (m), 683 (m), 667 (m), 660 (m), 640 (m), 633 (m), 621 (m), 564 (m), 518 (w), 485 (m), 466 (m), 408 (m). HRMS found \( m/z \): 793.13281 [M⁺H]⁺; \( \text{C}_{49}\text{H}_{23}\text{N}_4\text{S}_4 \) requires: 793.13310.

3,3′′-Dihexyl-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-y1)-2,2′:5′:2′′-terpyridine-4-
the reaction mixture was extracted with dichloromethane, the organic phase was dried with MgSO₄, filtered off and evaporated. The crude product was purified by precipitation from concentrated THF solution by using hexane. Orange powder (3.4 g, 97%). ¹H NMR (400 MHz, d₅-CDCl₃) δ ppm 7.19 (d, J = 5.2, 2H, C2 or C3), 7.12 (d, J = 3.8, 2H, D3 or D4), 7.01 (d, J = 3.8, 2H, D5 or D6), 6.95 (d, J = 5.2, 2H, C5 or C6), 6.81–6.83 (m, 8H, –Ph), 3.90 (t, J = 6.6, 4H, Hex⁴), 3.76 (s, 6H, –OCH₃), 2.81 (t, J = 7.9, 4H, Hex⁵), 1.65–1.81 (m, 8H, Hex² + Hex⁶), 1.41–1.43 (m, 8H, Hex³ + Hex⁴). ¹³C NMR (101 MHz, d₅-CDCl₃) δ ppm 153.64, 153.27, 140.70, 140.09, 137.53, 137.07, 135.30, 126.85, 124.10, 115.41, 114.59, 84.18, 68.56, 55.71, 30.44, 29.29, 29.26, 29.12, 25.88, 24.75, 24.59. ¹³B NMR (128.3 MHz, d₅-CDCl₃) δ ppm 22.50. IR (DRIFT), cm⁻¹ 1309 (ω), 1299 (m), 1281 (s), 1261 (m), 1231 (s), 1181 (m), 1146 (s), 1123 (m), 1105 (m), 1095 (m), 1071 (m), 1039 (m), 1019 (m), 990 (m), 882 (m), 831 (m), 823 (m), 787 (s), 774 (m), 740 (m), 726 (m), 706 (w), 670 (w), 660 (w), 630 (m), 622 (m), 567 (w), 525 (w), 498 (w), 468 (w), 425 (w), 400 (m). HRMS found m/z: 765.21732 [M⁺Na⁺], C₄₂H₄₀O₂N₄S₄ requires: 765.21711.

5′′-[3′′,3′′′-Bis(6-(4-methoxyphenoxy)hexyl)-2,2′′,5′′,2′′′-quaterthiophene-5′,5′′′-diyl)bis(4′′,4′′′-tetracycloborane)]octaethylene) 3,3′′-Bis[(6-(4-methoxyphenoxy)hexyl)-2,2′′,5′′,2′′′-quaterthiophene-5′,5′′′-diyl)bis(4′′,4′′′-tetracycloborane)]octaethylene) 3,3′′-Bis[(6-(4-methoxyphenoxy)hexyl)-2,2′′,5′′,2′′′-quaterthiophene-5′,5′′′-diyl)bis(4′′,4′′′-tetracycloborane)]octaethylene). The crude product was purified by column chromatography (SiO₂, hexane/CH₂Cl₂, 1:1) to obtain the pure product (0.62 g, 48%). ¹H NMR (300 MHz, d₅-CDCl₃) δ ppm 7.29 (d, J = 5.4, 2H, D4 or D5), 6.96 (d, J = 5.1, 2H, D3 or D6), 6.82 (s, 8H, –Ph), 3.84 (t, J = 6.5, 4H, Hex⁴), 3.77 (s, 6H, –OCH₃), 2.52 (t, J = 7.7, 4H, Hex⁵), 1.74–1.67 (m, 4H, Hex⁶), 1.63–1.56 (m, 4H, Hex⁷), 1.44–1.29 (m, 8H, Hex³ + Hex⁴).

The crude product was purified by column chromatography (SiO₂, hexane/CH₂Cl₂, 1:1) to obtain the pure product (0.62 g, 48%). ¹H NMR (300 MHz, d₅-CDCl₃) δ ppm 7.29 (d, J = 5.4, 2H, D4 or D5), 6.96 (d, J = 5.1, 2H, D3 or D6), 6.82 (s, 8H, –Ph), 3.84 (t, J = 6.5, 4H, Hex⁴), 3.77 (s, 6H, –OCH₃), 2.52 (t, J = 7.7, 4H, Hex⁵), 1.74–1.67 (m, 4H, Hex⁶), 1.63–1.56 (m, 4H, Hex⁷), 1.44–1.29 (m, 8H, Hex³ + Hex⁴).
1154 (w), 1130 (w), 1109 (m), 1090 (m), 1073 (w), 1038 (s), 1016 (m), 1001 (m), 943 (w), 932 (m), 915 (m), 894 (m), 884 (m), 826 (s), 789 (w), 767 (w), 742 (s), 732 (m), 717 (s), 695 (m), 686 (m), 663 (m), 629 (m), 602 (w), 571 (w), 531 (m), 521 (m), 509 (w), 490 (w), 436 (w), 422 (w). HRMS found m/z: 579.25984 [M+H]⁺, C₃₄H₄₉O₈S₂ requires: 579.25973.

5.5′-(3′,3′-Bis(6-(4-methoxyphenox)hexyl)-2,2′-bithiophene-5,5′-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). 3.3′-Bis(6-(4-methoxyphenox)hexyl-2,2′-bithiophene-0.6 (g, 1 mmol), dtbpy (46 mg, 0.17 mmol) and [Ir(OMe)(COD)] (148 mg, 0.07 mmol) were placed in a tube and vacuum–argon cycles were applied. Tetrahydrofuran (15 mL), hexane (15 mL) and HBPin (0.6 mL, 0.53 g, 4.2 mmol) were added through septum. The tube was heated at 50 °C for 4 days. After opening the tube, water was added and the solution was stirred for an hour. Then the reaction mixture was extracted with dichloromethane, the organic phase was dried with MgSO₄, filtered off and evaporated to obtain the product (0.88 g, 100%). The product was used as obtained for the following synthesis without purification. ¹H NMR (300 MHz, d-CDCl₃) δ ppm 7.52 (s, 2H, D), 6.82 (s, 8H, -Ph), 3.85 (t, J = 6.5, 4H, Hex²), 3.77 (s, 6H, -OCH₃), 2.53 (t, J = 7.7, 4H, Hex¹), 1.72–1.68 (m, 4H, Hex²), 1.60–1.54 (m, 4H, Hex¹), 1.42–1.30 (m, 28H, Hex¹ + CH₃ pinacol ester). ¹³C NMR (101 MHz, d-CDCl₃) δ ppm 135.59, 135.25, 143.42, 138.71, 136.29, 128.71, 115.41, 114.58, 84.10, 68.55, 55.74, 30.56, 29.24, 29.10, 28.57, 25.82, 24.76. ¹¹B NMR (128.3 MHz, d-CDCl₃) δ ppm 22.48. IR (DRIFT), cm⁻¹: 3045 (w), 2977 (s), 2934 (s), 2857 (s), 2833 (m), 1615 (w), 1591 (m), 1532 (m), 1508 (s), 1470 (m), 1456 (s), 1435 (m), 1380 (m), 1373 (m), 1239 (m), 1296 (m), 1268 (m), 1232 (s), 1180 (w), 1167 (w), 1142 (s), 1107 (m), 1074 (w), 1039 (m), 984 (w), 961 (m), 925 (w), 853 (m), 825 (m), 802 (m), 773 (w), 742 (m), 723 (m), 686 (m), 665 (s), 605 (w), 578 (m), 523 (m), 436 (w). HRMS found m/z: 853.41211 [M+Na]⁺. C₃₆H₄₉O₈B₂Na₂ requires: 853.41209.

4′,3′-(3′,3′-Bis(6-(4-methoxyphenox)hexyl)-5,5′-diyl)-2′,2′′,2′′′-terpyridine-4′-yl)-2,2′,5′,2′′,5′′,2′′′-quaterphenophene Q4S-A. 4′-(5′-Bromothiophen-2-yl)-2′,2′′,2′′′-terpyridine-4′-yl)-2,2′,5′,2′′,5′′,2′′′-quaterphenophene Q4S-A. 4′-(5′-Bromothiophen-2-yl)-2′,2′′,2′′′-terpyridine-4′-yl)-2,2′,5′,2′′,5′′,2′′′-quaterphenophene Q4S-A. 4′-(5′-Bromothiophen-2-yl)-2′,2′′,2′′′-terpyridine-4′-yl)-2,2′,5′,2′′,5′′,2′′′-quaterphenophene Q4S-A. 4′-(5′-Bromothiophen-2-yl)-2′,2′′,2′′′-terpyridine-4′-yl)-2,2′,5′,2′′,5′′,2′′′-quaterphenophene Q4S-A. 4′-(5′-Bromothiophen-2-yl)-2′,2′′,2′′′-terpyridine-4′-yl)-2,2′,5′,2′′,5′′,2′′′-quaterphenophene Q4S-A.
MgSO₄ filtered and evaporated. The product was used in the following synthesis without purification (0.48 g, 94%). ¹H NMR (400 MHz, d₂-CDCl₃) δ ppm 7.43 (s, 2H, C1), 7.09 (s, 2H, D1), 6.78 (s, 8H, -Ph), 6.76 (s, 8H, -Ph), 3.87–3.81 (m, 8H, Hex3), 3.72 (s, 12H, -OCH3), 2.81 (t, J = 8.0, 4H, Hex), 2.60 (t, J = 7.6, 4H, Hex), 1.75–1.60 (m, 16H, Hex₂ + Hex), 1.48–1.40 (m, 16H, Hex3 + Hex4). ¹³C NMR (101 MHz, d₂-CDCl₃) δ ppm 154.22, 153.86, 143.53, 141.23, 138.16, 136.51, 131.09, 129.23, 128.37, 115.83, 115.04, 84.74, 68.32, 56.13, 30.92, 29.89, 26.42, 26.15, 25.14, 24.93. ¹¹B NMR (128 MHz, d₂-CDCl₃) δ ppm 22.39.

3',4',3'″-Tetra(6-(4-methoxyphenyl)hexyl)-5′″-bis(2,2′,6′,2″-terpyridin-4′-yl)-2,2′,5′,2″′-quateriophene Q4257-A. 5',5″′-(3,4,3″′-Tetra(6-(4-methoxyphenyl)hexyl)-2,2′,5′,2″′-quateriophene-5′″-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.45 g, 0.32 mmol), Brpy (0.215 g, 0.69 mmol), K₂CO₃ (0.40 g, 2.89 mmol) and PEPPSI-IrP (32 mg) were placed in a Schlenk tube and vacuum and three vacuum-argon cycles were applied. The reaction mixture was heated to 90 °C overnight. After cooling to room temperature the mixture was diluted with dichloromethane (40 mL) and washed with water (3 x 200 mL). The organic layer was dried with MgSO₄ filtered and evaporated to obtain the crude product. The product was purified by column chromatography (Al₂O₃, hexane/THF, 3 : 2). Orange solid (0.17 g, 33%).

¹H NMR (400 MHz, d₂-CDCl₃) δ ppm 8.74 (m, 4H, A1), 8.70 (s, 4H, B1), 8.67 (m, 4H, A₂), 7.91 (td, J = 7.7, J = 2.1, 4H, A₃), 7.67 (s, 2H, C1), 7.40–7.37 (m, 4H, A₄), 7.19 (s, 2H, D₁), 6.80–6.72 (m, 16H, -Ph), 3.90–3.83 (m, 8H, Hex6), 3.69 (s, 6H, -OCH₃), 3.66 (s, 6H, -OCH₃), 2.89 (t, J = 7.8, 4H, Hex), 2.66 (t, J = 7.8, 4H, Hex), 1.80–1.69 (m, 16H, Hex + Hex). ¹³C NMR (101 MHz, d₂-CDCl₃) δ ppm 151.66, 151.41, 154.23, 153.85, 149.74, 143.72, 143.37, 143.31, 139.47, 137.42, 136.23, 133.28, 129.58, 129.34, 128.46, 124.58, 121.62, 116.88, 115.83, 115.03, 69.06, 56.09, 31.06, 29.92, 29.70, 26.50, 26.42. IR (DRIFT), cm⁻¹ 3063 (w), 3009 (w), 2935 (s), 2854 (m), 1601 (m), 1581 (s), 1566 (s), 1508 (s), 1462 (s), 1400 (w), 1288 (w), 1238 (w), 1180 (w), 1149 (w), 1107 (m), 1072 (w), 1038 (s), 991 (w), 883 (w), 825 (m), 795 (m), 744 (m), 679 (w), 656 (s), 633 (w), 621 (w), 525 (w). HRMS found m/z: 1617.6568 [M⁺H][⁺], C₉₈H₁₀₁O₈N₆S₄ requires: 1617.6558.

**General procedure for bromination of A-unimers**

A unimer was dissolved in dichloromethane (to a concentration of ca. 0.02 M), the solution was then cooled in an ice bath and BBr₃ was added (excess). After 4 hours of stirring the cooling bath was removed and the solution was poured into water. The mixture was carefully neutralized with a saturated solution of K₂CO₃. Then the product was extracted with dichloromethane, dried with MgSO₄ filtered off and evaporated to obtain the desired product.

3,3″-Di(6-bromohexyl)-5′″-bis(2,2′,6′,2″′-terpyridin-4′-yl)-2,2′,5′,2″′-quateriophene Q2457-Br. Red solid (95%). ¹H NMR (400 MHz, d₂-CDCl₃) δ ppm 8.74 (m, 4H, A1), 8.71 (s, 4H, B₁), 8.68 (m, 4H, A₂), 7.92 (td, J = 7.8, J = 7.8, J = 1.8, 4H, A₃), 7.69 (s, 2H, C₁), 7.40 (dd, J = 7.7, J = 4.6, 4H, A₄), 7.19 (s, 2H, D₁), 3.46–3.41 (m, 8H, Hex6), 2.50 (m, 4H, Hex), 2.66 (m, 4H, Hex), 1.92–1.69 (m, 16H, Hex2 + Hex4), 1.55–1.47 (m, 16H, Hex + Hex). ¹³C NMR (101 MHz, d₂-CDCl₃) δ ppm 156.29, 155.97, 149.32, 143.22, 142.97, 140.85, 139.19, 137.0, 135.89, 132.87, 129.14, 128.95, 128.06, 124.22, 121.29, 116.53, 34.32, 33.00, 30.55, 29.71, 28.75, 28.22. IR (DRIFT), cm⁻¹ 3062 (m), 3012 (m), 2930 (s), 2855 (s), 1731 (w), 1656 (w), 1598 (s), 1582 (s), 1567 (s), 1543 (m), 1466 (s), 1453 (s), 1437 (m), 1401 (m), 1335 (w), 1278 (w), 1265 (m), 1236 (m), 1204 (w), 1192 (w), 1145 (w), 1124 (w), 1094 (m), 1071 (m), 1042 (m), 1014 (m), 990 (m), 971 (w), 936 (w), 883 (m), 865 (w), 847 (m), 837 (m), 820 (w), 791 (s), 773 (m), 743 (s), 730 (s), 712 (w), 676 (w), 660 (s), 633 (m), 622 (m), 564 (m), 540 (w), 500 (m), 467 (w), 403 (m). HRMS found m/z: 1441.1509 [M⁺H][⁺], C₇₀H₇₂N₆Br₃S₄ requires: 1441.1507.

**General procedure for quaternization of Br-unimers**

A unimer was dissolved in toluene (to a concentration of ca. 6.5 mM) and the flask was flushed with argon. Triethyl-
phosphine (P\textsubscript{Et\(_3\)}) was added as 1 M solution in THF (ca. 20 eq.) and the reaction was heated to 110 °C for 4 days during which the quaternized product gets precipitated from the solution. After cooling to room temperature the product was filtered and washed with toluene and diethyl ether. The desired product was dried in vacuo.

6,6′-[5′,5′′-Bis[2,2′:6′,2′′-terpyridine-4′-yl]-2,2′,5′,2″,5″,2‴-quaterthiophen-3,3‴-diyl]-bis(hexan-1,1′-diyl triethyl phosphonium) bromide Q247-P\(_P\). Red solid (74%). \(^1\)H NMR (400 MHz, \(d_4\)-CD\(_2\)OD) \(\delta\) ppm 8.60 (dd, \(J = 5.0, J = 1.4, 4H, A^3\)), 8.44 (dd, \(J = 7.9, 4H, A^4\)), 8.29 (s, 4 H, B^3), 7.89 (td, \(J_1 = 7.7, J_2 = 1.8, 4H, A^5\)), 7.47 (s, 2H, C^3), 7.39–7.45 (m, 4H, A^5), 7.12 (d, \(J = 3.6, 2H, D^3\) or D^4), 7.08 (d, \(J = 3.9, 2H, D^4\) or D^3), 2.78–2.87 (m, 4H, 4H, Hex^2 + Hex^3), 2.09–2.35 (m, 20H, P–CH\(_2\) + Hex^2 + Hex^3), 1.69–1.83 (m, 8H, Hex^2 + Hex^3), 1.10–1.34 (m, 22H, P–CH\(_2\)– + Hex^3). Due to the low solubility of this compound we were not able to obtain the \(^{13}\)C NMR spectrum in a suitable solvent.

\(^{31}\)P NMR (121.42 MHz, \(d_4\)-CD\(_2\)OD) \(\delta\) ppm 39.93. IR (DRIFT), \(\nu\) cm\(^{-1}\) 3062 (m), 3011 (m), 2975 (m), 2930 (s), 2858 (s), 1600 (s), 1592 (m), 1585 (m), 1573 (m), 1560 (m), 1544 (m), 1534 (m), 1522 (m), 1422 (m), 1363 (w), 1324 (w), 1292 (w), 1267 (m), 1234 (m), 1179 (w), 1158 (s), 1127 (s), 1108 (s), 1095 (s), 1018 (w), 991 (w), 887 (w), 845 (w), 795 (s), 744 (m), 660 (m), 621 (w), 509 (w), 471 (w), 455 (v). HRMS found \(m/z\): 399.20815 \(\left[\text{M}^+\right]\)\(^{13}\), C\(_{94}\)H\(_{132}\)N\(_6\)P\(_2\)S\(_4\) \(z = 4\) requires: 399.20812.

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References


