Conjugated metallo-supramolecular polymers containing a phosphole unit.

Tereza Vitvarová\textsuperscript{a,b}, Jan Svoboda\textsuperscript{b}, Muriel Hissler\textsuperscript{a*} and Jiří Vohlídal\textsuperscript{a,b}

\textsuperscript{a}Institut des Sciences Chimiques de Rennes, UMR6226 CNRS-Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France.

\textsuperscript{b}Charles University in Prague, Faculty of Science, Department of Physical and Macromolecular Chemistry, Hlavova 2030/8, CZ-128 43 Prague, Czech Republic.

Supporting Information Placeholder

Supporting Information

Scheme S1: Synthesis of unimer TPT starting from commercially available materials
Figure S1a): Electronic density contours and energy values for LUMO and HOMOs of TPT obtained using DFT calculations.
<table>
<thead>
<tr>
<th>LUMO</th>
<th>HOMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>– 2.160 eV</td>
<td>– 5.133 eV</td>
</tr>
</tbody>
</table>

HOMO –1
– 6.174 eV    

HOMO –2
– 6.177 eV    

HOMO –3
– 6.199 eV    

HOMO –4
– 6.758 eV    

**Figure S1b):** Electronic density contours and energy values for LUMO and HOMOs of T obtained using DFT calculations.
Figure S2: The solid-state luminescence spectra of unimers T, T34 and TPT and related Zn-polymers.

Next page contains the following figure

Figure S3: Off-resonance ($\lambda_{exc} = 780$ nm) Raman spectra of the TPT and related MSPs with various ion-couplers
Figure S4: Comparison of the calculated and measured IR and Raman spectra of TPT.

Next two pages show the following spectra

Figure S5: Raman spectra of P(TPT/Fe) taken with different excitation wavelengths

Figure S6: Infrared spectra of the TPT MSPs with various ion-couplers.
Figure S7. The UV/vis spectral changes at assembling of TPT with M\(^{2+}\) ions.
Figure S8. Luminescence spectral changes at assembling of TPT with M$^{2+}$ ions.
Figure S9. SEC record of the Ni$^{2+}$/TPT system ($r = 1$); inset: the UV/vis DAD spectrum of the apex fraction.

Figure S10. The UV/vis DAD spectra of SEC fractions of the Fe$^{2+}$/TPT system: Left: composition $r = 0.7$, different elution times, $t_{el}$. Right: fractions of dimers ($t_{el} = 1380$ s) present in the Fe$^{2+}$/TPT systems of different composition $r$.

Figure S11. Cyclic voltammetry of unimer TPT
Next 4 pages show the following spectra

**Figure S12:** $^1$H NMR of 1-phenyl-2,5-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaboralene-2-yl)thiophen-2-yl]thioxophosphole (2).

**Figure S13:** $^{13}$C NMR of 1-phenyl-2,5-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaboralene-2-yl)thiophen-2-yl]thioxophosphole (2)

**Figure S14:** $^1$H NMR of 1-phenyl-2,5-bis(5-tpy-thiophen-2-yl)thioxophosphole (TPT)

**Figure S15:** $^{13}$C NMR of 1-phenyl-2,5-bis(5-tpy-thiophen-2-yl)thioxophosphole (TPT)
1-phenyl-2,3-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)thioxophosphate (2)
1-phenyl-2,5-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaboralene-2-yl)]thiioxophosphole (2)
1-phenyl-2,5-bis(5-phenylthiophen-2-yl)thiophosphole (TPT)