Supporting Information

Ternary cooperative assembly—polymeric condensation of photoactive viologen, phosphonate-terminated dendrimers and crystalline anatase nanoparticles

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S1 : Experimental section

General: Chemicals were purchased from Sigma-Aldrich or Strem and used without further purification; solvents were dried and distilled by routine procedures. $\text{Vio}_1, \text{Vio}_2$ and $\text{Vio}_3$ were synthesized using published procedures. $^{13}\text{C}$ and $^{31}\text{P}$ CP MAS NMR spectra were acquired on a Bruker Avance 400 WB spectrometer operating at 100 MHz and 162 MHz respectively under cross-polarization conditions. Fourier transformed infrared (FTIR) spectra were obtained with a Perkin-Elmer Spectrum 100FT-IR spectrometer on neat samples (ATR FT-IR). Nitrogen sorption isotherms at 77 K were obtained with a Micromeritics ASAP 2010 apparatus. Prior to measurement, the samples were degassed for 8 h at 120 °C. The surface area ($S_{BET}$) was determined from BET treatment in the range 0.04–0.3 $p/p_0$ assuming a surface coverage of the nitrogen molecule estimated to be 13.5 Å. X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance Bruker AXS system using Cu$K\alpha$ radiation with a step size of 0.02° in the 2θ range from 0.3 to 10° for SAXS, and from 0.45 to 87° for WAXS (geometry: Bragg-Brentano, 0/2θ mode). DRUV spectra were measured in the 200–800 nm range using spectralon as the reference on a Perkin-Elmer Lambda 1050 spectrometer equipped with an integrating sphere (Laphsphere, North Sutton, USA). Scanning electronic microscopy (SEM) images were obtained using a JEOL JSM 6700F Transmission electronic microscopy (TEM) images were obtained using JEOL JEM 2010 at an activation voltage of 200 kV.

Material synthesis:

Path A. a phosphonate-terminated fourth generation dendrimer $\text{DG}_4$ was solubilised in an ethanol:water solution (5:2 volume ratio). Then, Ti(OiPr)$_4$ in a 1:20 molar ratio ([terminal organophosphonate] : [Ti]) was added to the transparent dendritic solution at room temperature. Upon addition, the solution became cloudy through polymerisation of the titanium alkoxide precursor. After 15 min of stirring, the precursor viologen ($\text{Vio}_1$, $\text{Vio}_2$ or $\text{Vio}_3$) in a {2.53 : 97.47 $\text{DG}_4$ : $\text{Vio}_1$, 16.42 : 83.58 $\text{DG}_4$ : $\text{Vio}_2$, 28.67 : 71.33 $\text{DG}_4$ : $\text{Vio}_3$} molar ratio was added and the resulting solution was heated at 60°C for 10 hours. After filtration and extensive washing of the precipitate with ethanol, the collected solids were dried at 60 °C for 2 hours given rise to $\text{M}_1$, $\text{M}_2$ and $\text{M}_3$ respectively.

Path B. a phosphonate-terminated fourth generation dendrimer $\text{DG}_4$ and viologen ($\text{Vio}_1$, $\text{Vio}_2$ or $\text{Vio}_3$) in a 2.53 : 97.47 $\text{DG}_4$ : $\text{Vio}_1$, 16.42 : 83.58 $\text{DG}_4$ : $\text{Vio}_2$, 28.67 : 71.33 $\text{DG}_4$ : $\text{Vio}_3$} molar ratio were solubilised in an ethanol : water solution (5:2 volume ratio). Then, Ti(OiPr)$_4$ in a 1:20 molar ratio ([terminal organophosphonate of $\text{DG}_4$] : [Ti]) was added to the yellow solution at room temperature. The resulting solution was heated at 60°C for 10 hours. After filtration and extensive washing of the precipitate with ethanol, the collected solids were dried at 60°C for 2 hours given rise to $\text{M}_1$, $\text{M}_2$ and $\text{M}_3$ respectively.

Path C. a phosphonate-terminated fourth generation dendrimer $\text{DG}_4$ was solubilised in an ethanol:water solution (5:2 volume ratio). Then, Ti(OiPr)$_4$ in a 1:20 molar ratio
([terminal organophosphonate] : [Ti]) was added to the transparent dendritic solution at room temperature. After 15 min of stirring, the viologen (Vio₁, Vio₂ or Vio₃) in a [2.53 : 97.47 [DG₄] : [Vio₁], 16.42 : 83.58 [DG₄] : [Vio₂], 28.67 : 71.33 [DG₄] : [Vio₃]) molar ratio was added and the resulting solution was heated at 100°C for 10 hours. After filtration and extensive washing of the precipitate with ethanol, the collected solids were dried at 60°C for 2 hours given rise to M₁, M₂ and M₃ respectively.

Path D. a phosphonate-terminated fourth generation dendrimer DG₄ was solubilised in an ethanol:water solution (5:2 volume ratio). Then, Ti(OiPr)₄ in a 1:20 molar ratio ([terminal organophosphonate] : [Ti]) was added to the transparent dendritic solution at room temperature. After 4 hours of stirring, the third sol-gel precursor (either Vio₁, Vio₂ or Vio₃) in a [2.53 : 97.47 [DG₄] : [Vio₁], 16.42 : 83.58 [DG₄] : [Vio₂], 28.67 : 71.33 [DG₄] : [Vio₃]) molar ratio was added and the resulting solution was heated at 60°C for 10 hours. After filtration and extensive washing of the precipitate with ethanol, the collected solids were dried at 60°C for 2 hours given rise to M₁, M₂ and M₃ respectively.

Typical example of preparation of supported gold nanoparticles Mₙ-Au)
To a suspension of Mₙ in ethanol was added a solution of HAuCl₄·3H₂O in ethanol. The mixture was sonicated for an hour at ambient temperature. To this suspension was added an aqueous solution of NaBH₄. The solution immediately turned purplish red. The reaction mixture was stirred for 2 hour at room temperature. After filtration, the solid was washed with deionized water and dried.

Table S1

<table>
<thead>
<tr>
<th>Material</th>
<th>S BET (m² g⁻¹)</th>
<th>P.D. (nm)</th>
<th>Anatase particle size (nm)</th>
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<tr>
<td>Path A</td>
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<tr>
<td>M₁</td>
<td>DG₄ + Ti(OiPr)₄ 15 min + Vio₁ (60°C)</td>
<td>342</td>
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<td>M₂</td>
<td>DG₄ + Ti(OiPr)₄ 15 min + Vio₂ (60°C)</td>
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<td>M₃</td>
<td>DG₄ + Ti(OiPr)₄ 15 min + Vio₃ (60°C)</td>
<td>122</td>
<td>3.7</td>
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<td>(Path B)</td>
<td>M₁</td>
<td>DG₄ + Ti(OiPr)₄ + Vio₁ (60°C)</td>
<td>155</td>
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<tr>
<td>M₂</td>
<td>DG₄ + Ti(OiPr)₄ + Vio₂ (60°C)</td>
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<td>3.9</td>
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<tr>
<td>M₃</td>
<td>DG₄ + Ti(OiPr)₄ + Vio₃ (60°C)</td>
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<td>(Path C)</td>
<td>M₁</td>
<td>DG₄ + Ti(OiPr)₄ + Vio₁ (100°C)</td>
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<td>M₂</td>
<td>DG₄ + Ti(OiPr)₄ + Vio₂ (100°C)</td>
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<tr>
<td>M₃</td>
<td>DG₄ + Ti(OiPr)₄ + Vio₃ (100°C)</td>
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<td>3.6</td>
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<td>(Path D)</td>
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<td>DG₄ + Ti(OiPr)₄ + Vio₁ (60°C)</td>
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<td>M₂</td>
<td>DG₄ + Ti(OiPr)₄ + Vio₂ (60°C)</td>
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<td>M₃</td>
<td>DG₄ + Ti(OiPr)₄ + Vio₃ (60°C)</td>
<td>90</td>
<td>3.6</td>
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*a Specific surface area. *b Average pore diameter (BJH). *c Average crystallite size estimated from the broadening of the [101] reflexion using the Debye–Scherrer equation.

Figure S2. DRIFT spectra of hybrid materials
Figure S2a. DRIFT spectra of hybrid materials ((Path A)

Figure S2b. DRIFT spectra of hybrid materials (Path B, C and D)
Path C

Transmittance %

Wavenumber (cm⁻¹)

M1
M3
M2

Path D

Transmittance %

Wavenumber (cm⁻¹)

M1
M3

1636 cm⁻¹
CH=N

1048 cm⁻¹
P–O–T

1636 cm⁻¹
CH=N

1048 cm⁻¹
P–O–T
Figure S3. Typical CP $^{13}\text{C}$ and CP $^{31}\text{P}$ MAS NMR (Path A).

Figure S3a. CP $^{31}\text{P}$ MAS NMR (Path A).
Figure S3b. CP $^{13}$C MAS NMR (Path A).

CP 1H13C M1
Table S2

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<tr>
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<th>$^{31}$P NMR (ppm)</th>
<th>$^{13}$C NMR (ppm)</th>
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<tr>
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<td>(N$_3$P$_3$)$_a^b$</td>
<td>(P=S)$_a^b$</td>
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<td></td>
<td>[-P(O)(Ti-O)$_2$]$_a^b$</td>
<td>N-CH$_3^a$</td>
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<td>M$_1$</td>
<td>61.18</td>
<td>18.28</td>
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<td>M$_2$</td>
<td>60.68</td>
<td>16.70</td>
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<tr>
<td>M$_3$</td>
<td>66.18</td>
<td>16.94</td>
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* signal belonging to dendrimer G$_4$

* signal belonging to viologen units

* overlaps with the side band
Figure S4. HRTEM of hybrid materials (path A)

TEM of M₁ (path A):
Figure S5. DRUV spectra of hybrid materials.
Figure S6. Typical SEM and HRTEM of M₁ to M₃ obtained by B, C and D paths.

SEM of M₂ (path B):

SEM of M₃ (path B):

SEM of M₁ (path C):

SEM of M₃ (path C):
SEM of $M_3$ (path C):

TEM of $M_1$ (path B):

TEM of $M_3$ (path B):

TEM of $M_1$ (path C):
TEM of $M_1$ (path D):
Figure S7. Nitrogen sorption analysis (Path B, C and D)

Figure S7a. Nitrogen sorption analysis (Path B)

Figure S7b. Nitrogen sorption analysis (Path C)

Figure S7c. Nitrogen sorption analysis (Path D)
Figure S8. X-ray diffraction of hybrid materials.

Path B
- M1
- M3
- M2

Path C
- M1
- M3
- M2

Path D
- M1
- M3
- M2
Figure S9. DRUV spectra of hybrid materials M₃-Au.

The difference seen between M₃-Au (Top) and it’s molecular version, namely the typical shoulder, arises from the electronic communication between Au, crystalline TiO₂ and viologen units in the hybrid material framework.