Electronic Supplementary Information

Peripheral functionalisation of dendrimers with polyoxotungstate complexes assembled by ionic bonding and their use as oxidation catalysts: Influence of the tether length.

Sylvain Nlate*, Lauriane Plault, Didier Astruc*

Spectroscopic characterization of intermediates compounds for the synthesis of dendritic POM complexes

Nona-allyl dendrimer **2,** nona-ol dendrimer **3** and nona-iodo dendrimer **4** were obtained using the procedure described in references 14.

Nona-ammonium nona-iodide dendritic salt 5. A mixture of nona-iodo dendrimer **4** (640 mg, 0.39 mmol) and tri-*n*- hexylamine (6 ml, 17 mmol) in CH_3CN was stirred for 12 h at 80 °C. After removal of the solvent under vacuum, the residue was washed with pentane and dissolved in 2 ml of CH_3CN. The product was precipitated with 30 ml of pentane and dried under vacuum to yield the dendritic salt **5** (0.789 g, 64%). The nona-iodo salt **5** was used without further purification, after NMR characterization. ^1H NMR (200 MHz, $CDCl_3$) δ_{ppm}: 3.6-3.4 (m_{broad}, N-CH_2), 1.79-1.70 (m_{broad}, N-CH_2-CH_2), 1.32 (m, CH_2), 0.88 (m, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ_{ppm}: 59.5 (CH_2-N), 31.1 (CH_2-CH_2-N), 26.3, (CH_2-C_q), 23.0, (CH_2), 22.2 (CH_2), 13.7 (CH_3).

Nona-ammonium nona-tetrafluoroborate dendritic salt 6. $AgBF_4$ (1.3 g, 6.65 mmol) was added into an ethanol solution of ammonium salt **5** (1 g, 0.246 mmol). The salt AgI immediately precipitated, and the mixture was stirred at room temperature for 10 h. After removal of AgI by filtration, the ethanol solution was evaporated and the residue was extracted with CH_2Cl_2. The solvent was then removed under vacuum, yielding the ammonium BF_4^- salt **6** (899 mg, 98%). This salt was also used without further purification, after NMR characterization. ^1H NMR (200 MHz, $CDCl_3$) δ□□□: 3.11 (m_{broad}, N-CH_2), 1.60 (m_{broad}, N-CH_2-CH_2), 1.31 (m, CH_2), 0.89 (m, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ□□□: 53.5 (CH_2-N), (CH_2-CH_2-N), 26.1 (CH_2-C_q), 23.4 (CH_2), 22.3 (CH_2), 13.8 (CH_3). RMN ^{19}F ($CDCl_3$ 188 MHz) δ□□□: -151,3 ppm (BF_4^-).

Intermediate derivatives for the synthesis of the bis(POM) dendrimer 10:

Hexa-allyl dendrimer 10a: Dendrimer **10a** was obtained as a colorless solid in 60% yield from the complex [CpFe(η^6-*p*-xylene)][PF_6], as in the procedure described in references 14 and 16.

Hexa-ol dendrimer 10b: The hexa-ol **10b** was obtained as a colorless solid in 68% yield from **10a**, as in the procedure described in references 14 and 16, and used without further purification. ^{1}H NMR (200 MHz, methanol d^4) δ_{ppm}: 7.0 (m, 4H, H_{arom}), 3.46 (t, 12H, HO-CH_2), 1.69 (m, 12H, HO-CH_2-CH_2), 1.35 (m, 12H, C_q-CH_2). ^{13}C NMR (63 MHz, methanol d^4) δ_{ppm}: 145 ($C_{q\ arom}$), 127 (CH_{arom}), 63.6 (CH_2-OH), 43.0 (C_q-CH_2), 34.7 (CH_2-CH_2-OH), 26.3 (C_q-CH_2). Elemental analysis calcd for $C_{24}H_{46}O_6$: C, 68.69; H, 10.20. Found: C, 68.13; H, 10.03%.

Hexa-iodo dendrimer 10c: The iodo dendrimer **10c** was obtained as a colorless solid in 54% yield from the hexa-ol **10b** using the procedure described in references 14 and 16. ^{1}H NMR (200 MHz, $CDCl_3$) δ_{ppm}: 7.0 (m, 4H, H_{arom}), 3.17 (t, 12H, I-CH_2), 1.78 (m, 12H, I-CH_2-CH_2), 1.64 (m, 12H, C_q-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$) δ_{ppm}: 143.4 ($C_{q,\ arom}$), 126.2 (CH_{arom}), 42.0 (C_q-CH_2), 38.3 (CH_2-CH_2-I), 27.5 (Cq-CH_2), 7.7 (CH_2-I). Elemental analysis calcd for $C_{26}H_{40}I_6$: C, 28.03; H, 3.62. Found: C, 28.03; H, 3.79%.

Hexa-ammonium hexa-iodide dendritic salt 10d: The dendritic salt **10d** was obtained from **10c** in 81% yield using the procedure described above for **5**, and used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$) δ_{ppm}: 3.8-3.6 (m_{broad}, N-CH_2), 1.71 (m, N-CH_2-CH_2), 1.31 (m, CH_2), 0.88 (m, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ_{ppm}: 59.7 (CH_2-N), 31.4 (CH_2-CH_2-N), 26.3, (CH_2-C_q), 23.5, (CH_2), 22.7 (CH_2), 14.3 (CH_3).

Hexa-ammonium hexa-tetrafluoroborate dendritic salt 10e: The dendritic salt **10e** was obtained from **10d** in 99% yield, using the procedure described for **6**, and used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$) δ_{ppm}: 7.3 (m, 4H, H_{arom}), 3.3 (m_{broad}, N-CH_2), 2.0 (m_{broad}, N-CH_2-CH_2), 1.37 (m, CH_2), 0.93 (m, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ_{ppm}: 59.5 (CH_2-N), 31.9 (CH_2-CH_2-N), 26.7 (CH_2-C_q), 24.1 (CH_2), 22.4 (CH_2), 14.3 (CH_3).

Intermediate derivatives for the synthesis of the tris(POM) dendrimer 11:

Tri-allyl dendrimer 11a: Allyl dendrimer **11a** was obtained from the [CpFe(toluene)][PF_6] complex as a colourless solid in 55% yield, as using the procedure described in references 14 and 16, and checked by NMR before use. ^{1}H NMR (200 MHz, $CDCl_3$) δ_{ppm}: 7.29 and 7.27 (m, 5H, H_{arom}), 5.63 (m, 3H, CH=CH_2), 5.15-5.13 (m, 6H, CH=CH_2), 2.57 (d, 6H, CH_2).

Tri-ol dendrimer 11b: The tri-ol **11b** was obtained as a colorless solid in 84% yield from the tri-allyl **11a**, using the procedure described in references 14, and checked by NMR before use. ^{1}H NMR (200 MHz, methanol d^4) δ_{ppm}: 7.31 and 7.18 (m, 5H, H_{arom}), 3.46 (t, 6H, HO-CH_2), 1.75 (m, 6H, CH_2), 1.30 (m, 6H, C_q-CH_2).

Tri-iodo dendrimer 11c: This dendrimer was obtained as a colorless solid in 93% yield from **11b** using the procedure described in references 14, and checked by NMR before use. ^{1}H RMN ($CDCl_3$, 200 MHz) δ_{ppm}: 7.35 (m, 5H, H_{arom}), 3.17 (t, 6H, CH_2-I), 1.85 (m, 6H, CH_2-CH_2-I), 1.62 (m, 6H, C_q-CH_2). ^{13}C RMN ($CDCl_3$, 63 MHz) δ_{ppm}: 146.4 ($C_{q,\ arom}$), 128.3-126.3 (CH_{arom}), 42.2 (CH_2-C_q), 38.3 (CH_2-CH_2-I), 27.4 (C_q-CH_2), 7.7 (CH_2-I).

Tri-ammonium tri-iodide salts dendrimer 11d: This salt was obtained from **11c** in 89% yield using the procedure described for **5**, and used without further purification. ^{1}H RMN ($CDCl_3$, 200 MHz) δ_{ppm}: 7.4 (m, 5H, H_{arom}), 3.3 (m_{broad}, CH_2-N), 1.3 (m_{broad}, CH_2), 0.9 (s, CH_3). ^{13}C RMN ($CDCl_3$, 63 MHz) δ_{ppm}: 145.2 ($C_{q,\ arom}$), 128.9 (CH_{arom}), 127.4 (CH_{arom}), 126.6 (CH_{arom}), 61.0 (CH_2-N), 31.9 (CH_2-CH_2-N), 26.4 (CH_2-C_q), 22.8 (CH_2), 22.2 (CH_2), 14.3 (CH_3).

Tri-ammonium tri-tetrafluoroborate dendritic salt 11e: The tetrafluoroborate salt **11e** was obtained from **11d** in 98% yield using the procedure described for **6,** and used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$) δ_{ppm}: 3.32 (m_{broad}, N-CH_2), 1.79 (m_{broad}, N-CH_2-CH_2), 1.31 (m, CH_2), 0.93 (m, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ_{ppm}: 145.2 ($C_{q,\ arom}$), 128.9-127.5-126.6 (CH_{arom}), 59.55 (CH_2-N), 31.6 (CH_2-CH_2-N), 26.4 (CH_2-C_q), 23.4 (CH_2), 22.3 (CH_2), 14.3 CH_3. ^{19}F RMN ($CDCl_3$ 188 MHz) δ_{ppm}: -151,3 ppm (BF_4^-).

Intermediate derivatives for the synthesis of the tetra(POM) dendrimer 17:

Dodeca-allyl dendrimer 12: The dodeca-allyl dendrimer 12 was obtained in 55% yield, from the iron dodeca-allyl complex reported in reference 16 using the procedure described in reference 14.

Dodeca-ol dendrimer 13: Dodeca-ol **13** was obtained as a colorless solid in 74% yield from **12** using the procedure described in references 14 and 16, and characterized by NMR before use. ^{1}H NMR (200 MHz, methanol d^4) δ_{ppm}: 7.33 (m, 6H, H_{arom}), 3.50 (t, 24H, HO-CH_2), 1.76 (m, 24H, HO-CH_2-CH_2), 1.35 (m, 24H, C_q-CH_2). ^{13}C NMR (63 MHz, methanol d^4) δ_{ppm}: 147 ($C_{q,\ arom}$), 123.7 and 122.9 (CH_{arom}), 62.2 (CH_2-OH), 42.5 (C_q-CH_2), 33.5 (CH_2-CH_2-OH), 26.7 (C_q-CH_2).

Dodeca-iodo dendrimer 14: Dendrimer **14** was obtained as a colourless solid in 20% yield from dodeca-ol **13**, using the procedure described in references 14, and characterized by

NMR before use. ^{1}H NMR (200 MHz, $CDCl_3$) δ_{ppm}: 7.33 (m, 6H, H_{arom}), 3.18 (t, 24H, I-CH_2), 1.84 (m, 24H, I-CH_2-CH_2), 1.62 (m, 24H, C_q-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$) δ_{ppm}: 144 ($C_{q, arom}$), 122 (CH_{arom}), 41.4 (C_q-CH_2), 37.2 (CH_2-CH_2-I), 26.4 (C_q-CH_2), 7.0 (CH_2-I).

Dodeca-ammonium dodeca-iodide dendritic salt 15: Dodeca-iodo salt **15** was obtained from **14** in 93% yield using the procedure described for **5**, and characterized by NMR before use ^{1}H NMR (200 MHz, $CDCl_3$) δ_{ppm}: 7.25 (s, 6H, H_{arom}), 3.34 (m_{broad}, N-CH_2), 1.75-1.64 (m_{broad}, N-CH_2-CH_2), 1.27 (m_{broad}, CH_2), 0.88 (m, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ_{ppm}: 59.1 (CH_2-N), 31.1 (CH_2-CH_2-N), 26.3 (CH_2-C_q), 25.9 (CH_2), 23.0, (CH_2), 22.3 (CH_2), 13.7 (CH_3).

Dodeca-ammonium dodeca-tetrafluoroborate dendritic salt 16: Dodeca-tetrafluoroborate salt **16** was obtained from **15** in 93% yield using the procedure described for **6,** and used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$) δ_{ppm}: 7.25 (s, 6H, H_{arom}), 3.34 (m_{broad}, N-CH_2), 1.79-1.73 (m_{broad}, N-CH_2-CH_2), 1.27 (m_{broad}, CH_2), 0.88 (m, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ_{ppm}: 59.1 (CH_2-N), 31.1 (CH_2-CH_2-N), 26.3 (CH_2-C_q), 25.9 (CH_2), 23.0, (CH_2), 22.3 (CH_2), 13.7 (CH_3).

Attempt to prepare the tetra(POM) dendrimer containing spacer groups between the arene core and dendritic tripod units:

Dodeca-allyl dendrimer 33: Dodeca-allyl **33** was obtained as a white solid in 85% yield using the procedure described for **19**. ^{1}H NMR ($CDCl_3$, 200.16 MHz) δ_{ppm}: 7.72 (s, 2H, Ar), 7.23 (d, 8H, Ar), 6.90 (d, 8H, Ar), 5.59 (m, 12H, CH=CH_2), 5.22 (s, 8H, CH_2O), 5.09 (m, 24H, CH=CH_2), 2.46 (d, 24H, CH_2CH=CH_2). ^{13}C NMR ($CDCl_3$, 62.91 MHz) δ_{ppm}: 156.47 (C_q, ArO), (C_q, $_{arom}$), 135.39 (C_q, $_{arom}$), 134.55 (CH=CH_2), 129.59 (C_q, $_{arom}$), 127.69 (CH_{arom}), 117.49 (CH=CH_2), 114.20 (CH_{arom}), 67.57 (CH_2O), 41.89 (C_q-CH_2), 41.77 (CH_2).

Dodeca-ol dendrimer 34: Dodeca-ol **34** was obtained as a colorless solid in 82% yield from dodeca-allyl **33** using the procedure described in references 14. ^{1}H NMR (CD_3OD, 200.16 MHz) δ_{ppm}: 7.67 (s, 2H, Ar), 7.26 (d, 8H, Ar), 6.92 (d, 8H, Ar), 5.16 (s, 8H, CH_2O), 3.46 (t, 24H, CH_2O), 1.68 (m_{braod}, 24H, CH_2), 1.28 (m_{broad}, 24H, CH_2). ^{13}C NMR (CD_3OD, 62.91 MHz) δ_{ppm}: 156.34 (C_q, ArO), 139.46 (C_q, $_{arom}$), 135.32 (C_q, $_{arom}$), 127.23 (CH_{arom}), 114.02 (CH_{arom}), 69.20 (CH_2O), 62.13 (CH_2O), 41.44 (C_q-CH_2), 33.28 (CH_2), 26.39 (CH_2). Elemental analysis calcd for $C_{74}H_{110}O_{16}$: C, 70.18; H, 8.83. Found: C, 71.00; H 9.22.