Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Organophosphonate Bridged Anatase Mesocrystals: Low Temperature Crystallization, Thermal Growth and Hydrogen Photo-Evolution

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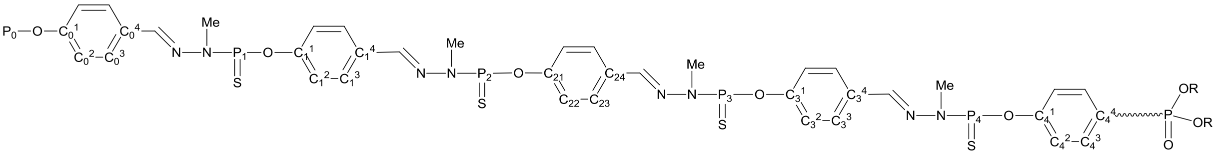
S1 : Experimental section

S1a. General: All manipulations were carried out with standard high-vacuum and dry-argon techniques. Chemicals were purchased from Sigma-Aldrich or Strem and used without further purification; solvents were dried and distilled by routine procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 25°C with Bruker AV 300, DPX 300 or AMX 400 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR and SiMe4 for ^{1}H and ^{13}C δNMR. ^{13}C and ^{31}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. Thermogravimetric analysis (TGA) was performed on a Pfeiffer Vacuum instrument at a heating rate of 10°C/min under a flow of nitrogen. X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance Bruker AXS system using CuKα 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, θ/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 (Lapshere, 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.

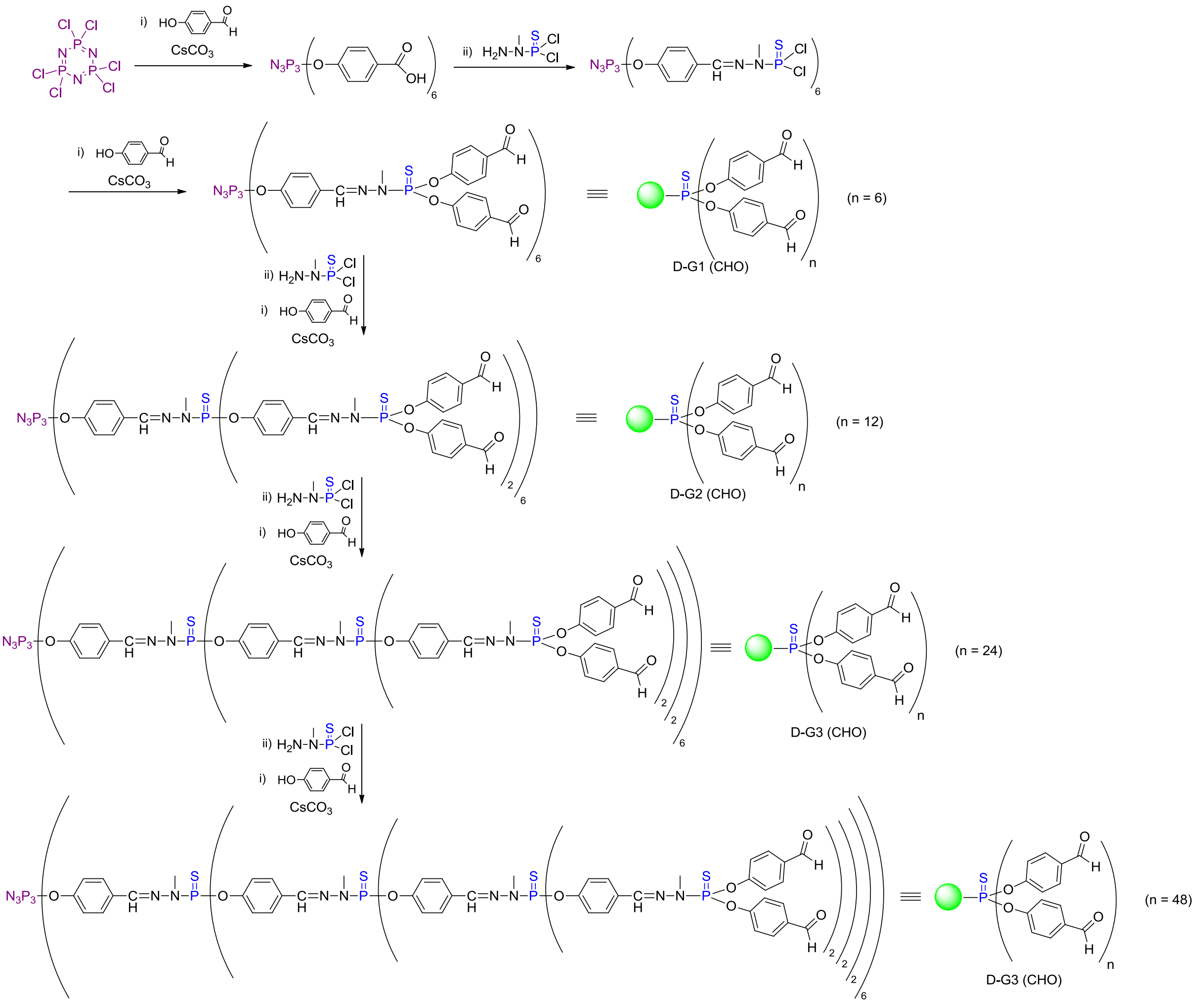
The numbering used for NMR:



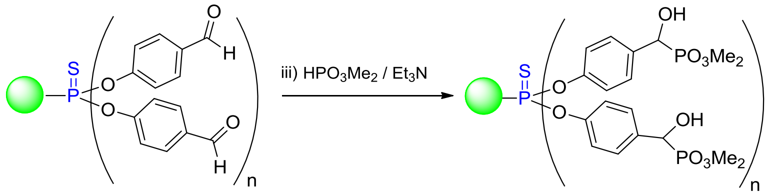
S1b. Synthesis of DG2, DG3, DG4 and Branch

a) General procedure for Synthesis of dendrimers with terminal aldehyde function D-Gn(CHO) (n = 1-4):

The reaction of hexachlorocyclotriphosphazene core with hydroxybenzaldehyde in basic conditions and then the condensation of the aldehyde groups with a phosphorhydrazide afford the dendrimer of generation one. The repetition of both steps was carried out until the obtaining of the fourth generation. [1]



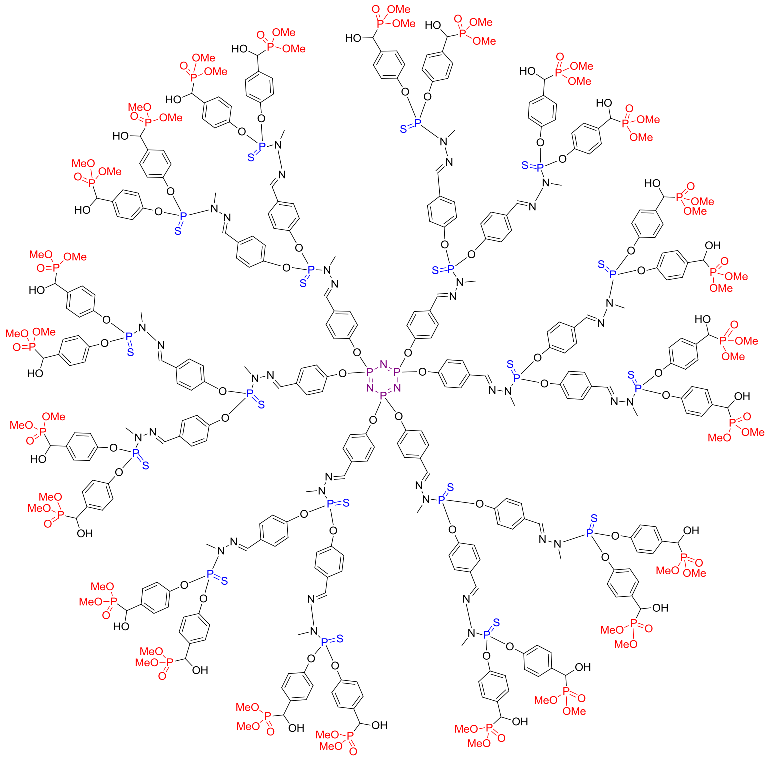
b) General procedure for the synthesis of dendrimers D-Gn(PO(OMe)2) (n = 2-4):



n = 12 : D-G2 (CHO)
n = 24 : D-G3 (CHO)
n = 48 : D-G4 (CHO)

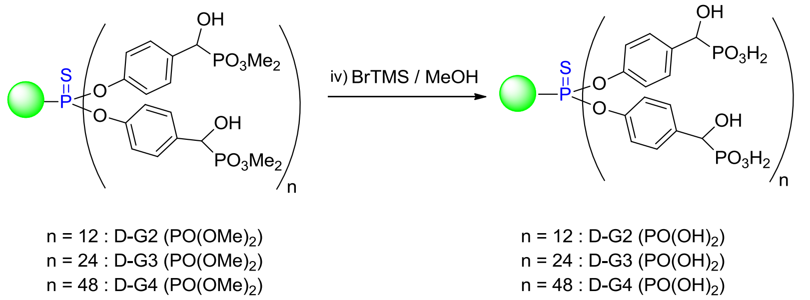
n = 12 : D-G2 $(PO(OMe)_2)$
n = 24 : D-G3 $(PO(OMe)_2)$
n = 48 : D-G4 $(PO(OMe)_2)$

One equivalent of D-Gn(CHO) (n = 2-4), (n = 2, 1.00 g, 0.146 mmol, n = 3, 0.20 g, $1.35\ 10^{-2}$ mmol; n = 4, 0.20 g, $6.50\ 10^{-3}$ mmol) was dissolved in THF (1 mL) then triethylamine (n = 2, 15 µL, 1.3 mmol; n = 3, 10 µL, 0.86 mmol, n = 4, 8 µL, 0.69 mmol) and dimethylphosphite (n = 2, 319 µL, 3.5 mmol; n = 3, 59 µL, 0.65 mmol, n = 4, 75 µL, 0.68 mmol) were added to the reaction mixture and left overnight under good stirring. The residue was washed by a mixture of THF/Et_2O (1/1) to afford the desired compound as a white powder.



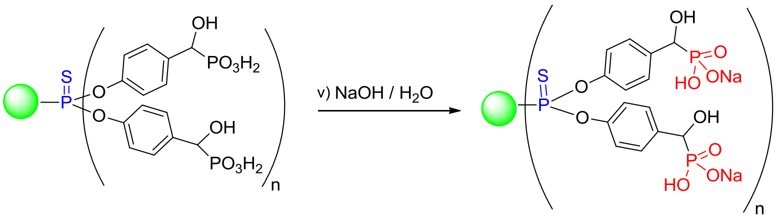
80% yield. ^{31}P-{^{1}H} NMR (DMSO d_6): δ = 11.7 (s, P_0), 27.10 (s, P(O)(O-CH_3)$_2$), 66.1 (s, $P_{1,2}$). ^{1}H NMR (DMSO d6): δ = 3.29 (d, $^{3}J_{HP}$ = 9.2 Hz, 54H, CH_3-N-P_1, CH_3-N-P_2), 3.49 (d, $^{2}J_{CP}$= 10.9 Hz, 72H, P(O)-O-CH_3), 3.55 (d, $^{2}J_{CP}$ = 10.6 Hz, 72H, P(O)-O-CH_3), 5.00 (dd, $^{3}J_{HH}$ = 5.4 Hz , $^{2}J_{HP}$ = 15.7 Hz, 24H, CH-P(O)), 6.30 (dd, $^{3}J_{HH}$ = 5.4 Hz, $^{2}J_{HP}$ = 15.7 Hz, 24H, OH), 7.0-8.0 (m, 186H, H_{arom}, CH=N). ^{13}C {^{1}H}NMR (DMSO d6): δ = 32.8 (d, $^{2}J_{CP}$ = 11.3 Hz, CH_3-N-$P_{1,2}$), 52.7 (d, $^{2}J_{CP}$ = 6.2 Hz, CH_3-O-P(O)), 53.2 (d, $^{2}J_{CP}$ = 6.3 Hz, CH_3-O-P(O)), 68.2 (d, $^{1}J_{CP}$ = 163.0 Hz, C-OH), 120.4 (s, C_2^{2}), 120.8 (br, C_0^{2}), 121.4 (s, C_1^{2}), 128.2 (s, C_0^{3}), 128.2 (s, C_1^{3}), 128.7 (d, $^{3}J_{CP}$ = 3.7 Hz, C_2^{3}), 132.1 (s, C_0^{4}), 132.1 (s, C_1^{4}), 135.4 (s, C_2^{4}), 140.2 (br, CH=N-N(Me)-$P_{1,2}$), 149.4 (d, $^{2}J_{CP}$ = 3.8 Hz, C_2^{1}), 150.4 (s, C_0^{1}), 150.7 (d, $^{2}J_{CP}$ = 6.4 Hz, C_1^{1}). IR: ν(OH) 3271 cm^{-1}.

c) General procedure for synthesis of dendrimers D-Gn(PO(OH)2) (n = 2-4):



At 0°C (ice bath) the bromotrimethylsilane (n = 2, 304 µL, 2.30 mmol; n = 3; 146 µL, 1.09 mmol; n = 4, 402 µL, 3.00 mmol), was added slowly to a suspension of dendrimer D-G_n(PO(OMe)$_2$) (n = 2, 0.30 g, 3.16 10^{-2} mmol; n = 3; 0.20 g, 10^{-2} mmol; n = 4, 0.30 g, 7.83 10^{-3} mmol) in acetonitrile (1.5 mL) and triethylamine (n = 2, 304 µL, 2.3 mmol; n = 3, 190 µL, 1.44 mmol ; n = 4, 317 µL, 2.4 mmol). The reaction mixture was left to react for 6 h at room temperature. Then the anhydrous methanol (2 mL) was added. After 2h, the reaction mixture was evaporated to dryness under reduced pressure. The residue was washed with water and ether and final compound was obtained as a white powder.

d) General procedure for synthesis of dendrimers D-Gn:

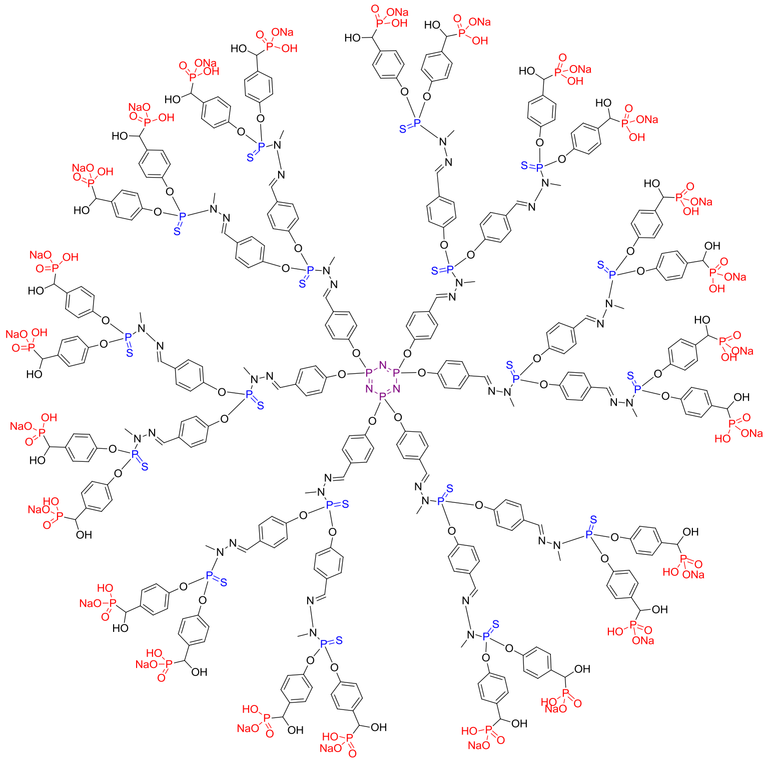


n = 12 : D-G2 (PO(OH)$_2$)
n = 24 : D-G3 (PO(OH)$_2$)
n = 48 : D-G4 (PO(OH)$_2$)

n = 12 : D-G2
n = 24 : D-G3
n = 48 : D-G4

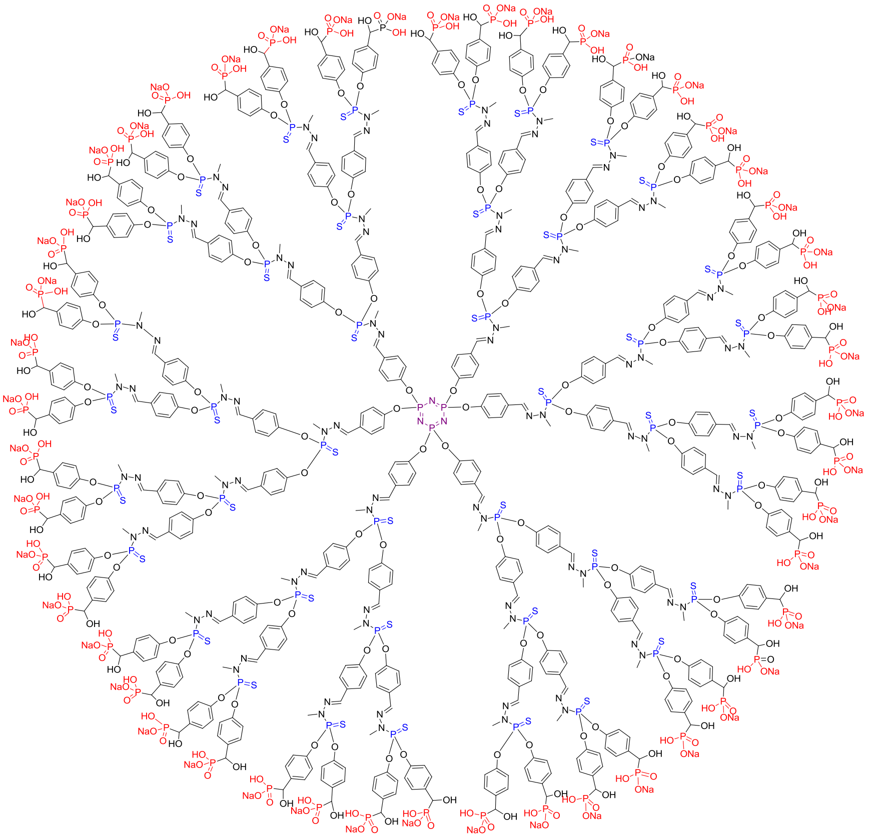
At 0°C, one equivalent of aqueous sodium hydroxide (0.1 M) per acid fonction was added slowly to a suspension of D-Gn(PO(OH)$_2$) in water. After one hour at room temperature, the clear solution was lyophilized to give the sodium monosalt dendrimer (D-Gn(PO(OH)O$^-$,Na$^+$) as a white powder.

D-G2:



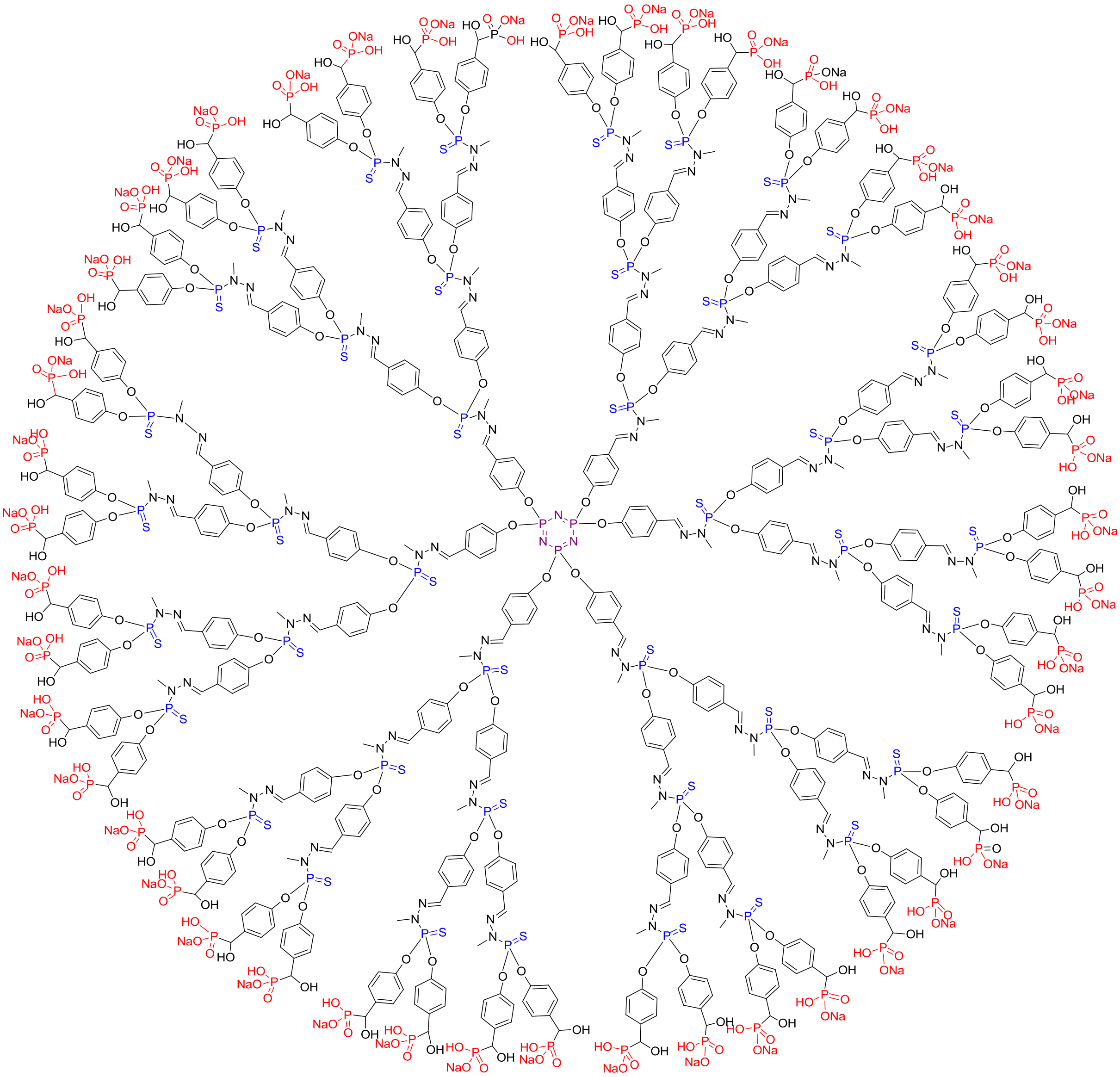
^{31}P {^{1}H} NMR (D$_2$O-DMSO-d$_6$, 161.99 MHz): δ = 15.8 (s, PO$_3$HNa), 64.2 (s, P$_1$, P$_2$) ; ^{13}C {^{1}H} NMR (D$_2$O-DMSO-d$_6$, 100.62 MHz): δ = 33.66 (CH$_3$-N-P$_{1,2}$), 71.67 (d, $^1J_{C\text{-}P}$ = 147.3 Hz, C$_2^5$), 120.55 (C$_2^2$), 128.77 (C$_2^3$), 138.35 (C$_2^4$), 148.98 (C$_2^1$).

D-G3:

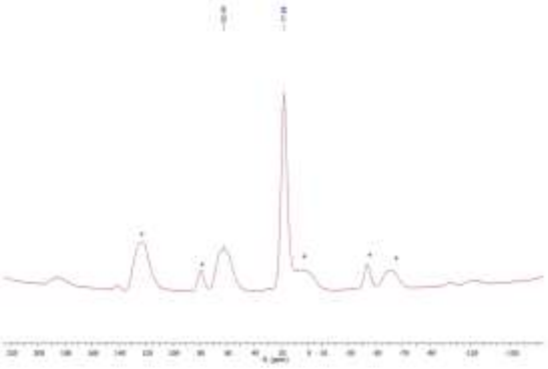


^{31}P {^{1}H} NMR (D_2O-DMSO-d_6, 121.5 MHz): δ = 15.56 (PO_3HNa), 63.49 (P_1, P_2, P_3). ^{13}C {^{1}H} NMR (D_2O-DMSO-d_6, 100.62 MHz): δ = 32.85 (CH_3-N-P_{1-3}), 71.49 (d, $^{1}J_{C-P}$ = 153.9 Hz, C_3^5), 120.45 (C_3^2), 128.81 (C_3^3), 138.43 (C_3^4), 148.95 (C_3^1).

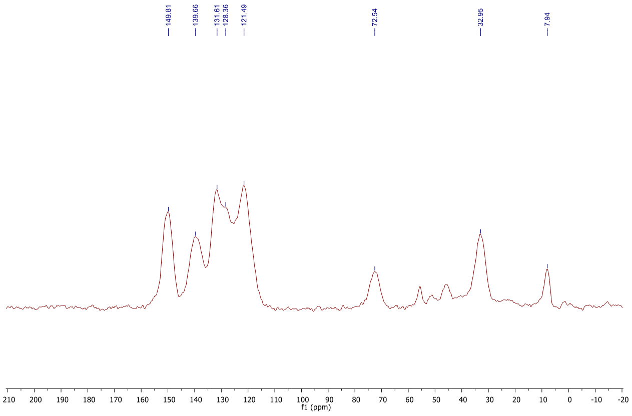
D-G4:



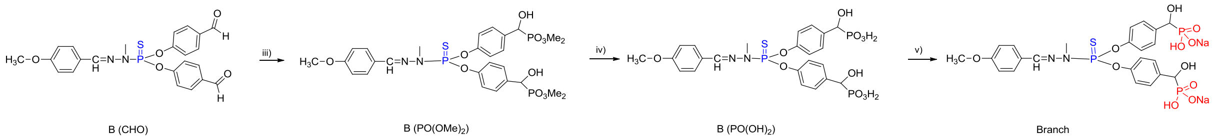
CP ^{1}H ^{31}P of D-G4



CP ^{1}H ^{13}C of D-G4



e) Synthesis of Branch:



To a solution of B(Cl_2) (1.00 g, 3.37 mmol) in THF (10 mL) were added 4-hydroxybenzaldehyde (0.90 g, 7.37 mmol) and cesium carbonate (3.29 g, 10.10 mmol). The mixture was stirred at room temperature for 10h. The mixture was filtered and evaporated. The residue was then dissolved in the minimum amount of $CHCl_3$ and precipitated with pentane. The resulting powder was filtered off and dried to afford B$(CHO)_2$ as a white powder in 96 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 60.60. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.40 (d, 3H, $^3J_{PH}$ = 11.1 Hz, N-CH_3), 3.86 (s, 3H, OCH_3), 6.94 (d, 2H, $^3J_{HH}$ = 8.7 Hz, H^2), 7.42 (dd, 4H, $^3J_{HH}$ = 8.5 Hz, $^4J_{PH}$ = 1.3 Hz, H^6), 7.63 (d, 2H, $^3J_{HH}$ = 8.9 Hz, H^3), 7.65 (s, 1H, CH=N), 7.89 (d, 4H, $^3J_{HH}$ = 8.6 Hz, H^7), 9.98 (s, 2H, CHO); ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.85 (d, $^2J_{CP}$ = 13.6 Hz, CH_3-N), 55.40 (OCH_3), 114.28 (C^2), 122.08 (d, $^3J_{CP}$= 5.0 Hz, C^6), 127.18 (C^4), 128.53 (C^3), 131.43 (d, $^4J_{CP}$= 1.0 Hz, C^7), 133.64 (d, $^5J_{CP}$= 1.6 Hz, C^8), 140.63 (d, $^3J_{CP}$ = 13.8 Hz, CH=N), 155.28 (d, $^2J_{CP}$= 7.2 Hz, C^5), 161.01 (C^1), 190.79 (CHO); DCI-MS (NH_3) m/z = 469.2 $[M+H]^+$.

To a solution of B$(CHO)_2$ (0.80 g, 1.71 mmol) in THF (1 mL) were added triethylamine (0.01 mL, 8.5 10^{-2} mmol) and dimethylphophite (0.35 mL, 3.76 mmol). The mixture left overnight under good stirring and then evaporated. The residue was dissolved in minimum of $CHCl_3$ and precipitated with pentane. The resulting powder was filtered off and the procedure was repeated twice to afford B$(PO(OMe)_2)$ as a white powder in 93% yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 23.26 (P=O), 62.42 (P=S). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (d, 3H, $^3J_{PH}$ = 10.7 Hz, N-CH_3), 3.62 (d, $^3J_{PH}$ = 10.4 Hz, 6H, P-OCH_3), 3.66 (d, $^3J_{PH}$ = 10.4 Hz, 6H, P-OCH_3OCH_3), 3.84 (s, 3H, OCH_3), 4.69 (s br, 2H, OH), 5.01(d, 2H, $^2J_{PH}$ = 11.2 Hz, CH-OH), 6.93 (d, 2H, $^3J_{HH}$ = 8.7 Hz, H^2), 7.23 (d, 4H, $^3J_{HH}$ = 8.1 Hz, H^6), 7.44 (d, 4H, $^3J_{HH}$ = 7.0 Hz, H^7), 7.61 (s, CH=N), 7.65 (d, 2H, $^3J_{HH}$ = 8.7 Hz, H^3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.90 (d, $^2J_{CP}$ = 13.1 Hz, CH_3-N), 53.73 (d, $^2J_{CP}$ = 7.3 Hz, P-OCH_3), 53.89 (d, $^2J_{CP}$ = 6.2 Hz, P-OCH_3), 55.37 (OCH_3), 69.91 (d, $^1J_{CP}$ = 161.2 Hz, CH-OH), 114.19 (C^2), 121.41 (s br, C^6), 127.61 (C^4), 128.30 (d, $^3J_{CP}$= 5.5 Hz, C^7), 128.45 (C^3), 133.66 (C^8), 139.74 (d, $^3J_{CP}$ = 13.8 Hz, CH=N), 150.52 and 150.55 (2d, $^2J_{CP}$= 7.2 Hz, C^5), 160.74 (C^1).

To a suspension of B$(PO(OMe)_2)$ (0.60 g 0.87 mmol) in acetonitrile (1.5 mL) and triethylamine (0.24 mL, 1.73 mmol) bromotrimethylsilane (0.48 mL, 3.64 mmol) was added slowly at 0°C. The reaction mixture was lstirred for 12 h at room temperature and then the anhydrous methanol (2 mL) was added. After 2h, the reaction mixture was evaporated to dryness under reduced pressure. The residue was washed water and ether and B$(PO(OH)_2)$ was obtained as a yellow powder with a yield of 75%. ^{31}P NMR (121 MHz, DMSO): δ = 17.41, 17.44 (P=O), 62.64 (P=S). ^{1}H NMR (300 MHz, DMSO) δ 3.32 (d, 3H, $^3J_{PH}$ = 11.0 Hz, N-CH_3), 3.78 (s, 3H, OCH_3), 4.54 (s br, 6H, OH), 4.65(d, 2H, $^2J_{PH}$ = 13.8 Hz, CH-OH), 7.01 (d, 2H, $^3J_{HH}$ = 8.8 Hz, H^2), 7.10 (d, 4H, $^3J_{HH}$ = 8.1 Hz, H^6), 7.40 (d, 4H, $^3J_{HH}$ = 7.3 Hz, H^7), 7.68 (d, 2H, $^3J_{HH}$ = 8.7 Hz, H^3), 7.91 (s br, CH=N); ^{13}C NMR (75 MHz, DMSO) δ 33.36 (d, $^2J_{CP}$ = 12.1 Hz, CH_3-N), 55.70 (OCH_3), 70.61 (d, $^1J_{CP}$ = 157.4 Hz, CH-OH), 114.76 (C^2), 120.31 (s, C^6), 127.94 (C^4), 128.76 (C^3), 129.06 (d, $^3J_{CP}$= 4.7 Hz, C^7), 138.39 (C^8), 141.64 (d,

$^{3}J_{CP}$ = 14.1 Hz, CH=N), 149.21 and 149.25 (2d, $^{2}J_{CP}$= 6.7 Hz, C^{5}), 160.77 (C^{1}); FAB-MS m/z = 655 [M+Na]$^{+}$, 633 [M+H]$^{+}$.

The sodium monosalt form was obtained by adding aqueous sodium hydroxide (0.1N, 7.00 mL, 0.70 mmol) to a suspension of B(PO(OH)$_2$) (0.44 g, 0.70 mmol) in water (16 mL) at 0°C. After 1h the solution was lyophilized to give B(PO(OH)O^{-},Na^{+}) as a white powder in 93% yield. ^{31}P NMR (121 MHz, D$_2$O): δ = 16.10, 16.12 (P=O), 64.58 (P=S). ^{1}H NMR (300 MHz, D$_2$O) δ 3.12 (d, 3H, $^{3}J_{PH}$ = 10.7 Hz, N-CH$_3$), 3.60 (s, 3H, OCH$_3$), 4.68 (d, 2H, $^{2}J_{PH}$ = 10.3 Hz, CH-OH), 6.77 (d, 2H, $^{3}J_{HH}$ = 8.5 Hz, H^{2}), 7.08 (d, 4H, $^{3}J_{HH}$ = 8.2 Hz, H^{6}), 7.35 (d, 4H, $^{3}J_{HH}$ = 7.7 Hz, H^{7}), 7.46 (d, 2H, $^{3}J_{HH}$ = 8.5 Hz, H^{3}), 7.60 (s br, CH=N). ^{13}C NMR (75 MHz, D$_2$O) δ 32.46 (d, $^{2}J_{CP}$ = 11.4 Hz, CH$_3$-N), 55.33 (OCH$_3$), 71.57 (d, $^{1}J_{CP}$ = 151.9 Hz, CH-OH), 114.22 (C^{2}), 120.80 (d, $^{3}J_{CP}$= 2.4 Hz, C^{6}), 127.29 (C^{4}), 128.57 (d, $^{3}J_{CP}$= 4.7 Hz, C^{7}), 128.69 (C^{3}), 137.50 (C^{8}), 142.46 (d, $^{3}J_{CP}$ = 14.3 Hz, CH=N), 149.16 and 149.20 (2d, $^{2}J_{CP}$= 7.2 Hz, C^{5}), 160.14 (C^{1}).

S1c. Synthesis of hybrid materials M1 to M15.

In a typical procedure for the material synthesis, phosphonated dendrimer (D-Gn(PO(OH)O^{-},Na^{+}) or D-G2(PO(OMe)$_2$)) was poured into a mixture of solvent-water (5/2 v:v) solution (solvent: Ethanol, Acetone or THF). After 15 minutes of stirring, titanium alkoxide precursor (Ti(OiPr)$_4$, Ti(OtBu)$_4$ or Ti(OiPr)$_2$(acac)$_2$) in the suited molar ratio ([dendrimer]: [Ti] = 1:5, 1:10 or 1: 20) was added to the transparent dendritic solution at room temperature. Upon addition, the solution became cloudy through polymerisation of the titanium precursor and the resulting solution was stirred at 25°C or heated at (60°C or 100°C) for 10 hours (or was sonicated for 2 hours). After filtration and extensive washing of the precipitate with ethanol, the collected solid was dried at 60°C for 2 hours.

S1d. Thermal annealing of hybrid materials.

For thermal treatment, the resulting hybrid dendrimer-titanium dioxide Mx materials are calcined for 2 hours at 500°C under air (rate 5°C/ min) to give Mx-500.

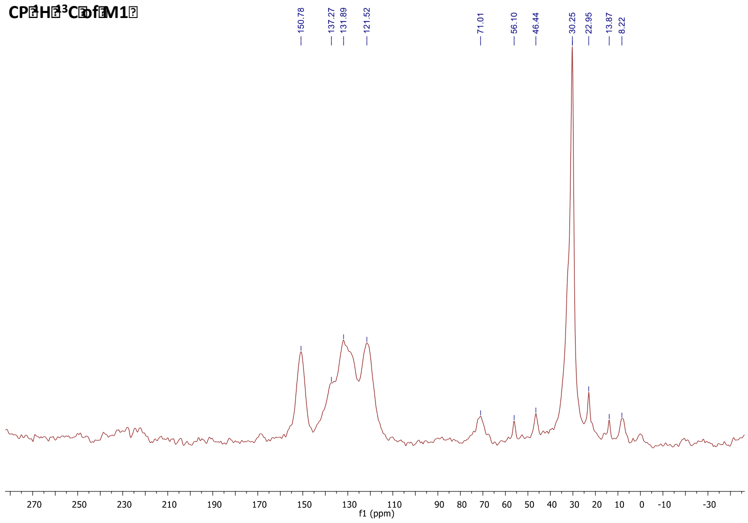
S1e. Water splitting photo-catalysis.

The amount of sample employed was 20 mg. The experiments were carried out in a quartz reactor. A solution consisting of 24 ml of water and 8 ml of methanol was used as the reaction media. The solution was purged with Ar for 30 min and after that the reactor was pressurized to 0.5 bar with Ar. The solution was kept at constant temperature (22 °C). A concentrate simulated solar light was employed as the source of light. The solar simulator consisted of a 1000 W Xe lamp equipped with an AM 1.5 filter. The amount of H$_2$ was measured by injecting 100 ml in a GC with a TCD detector.

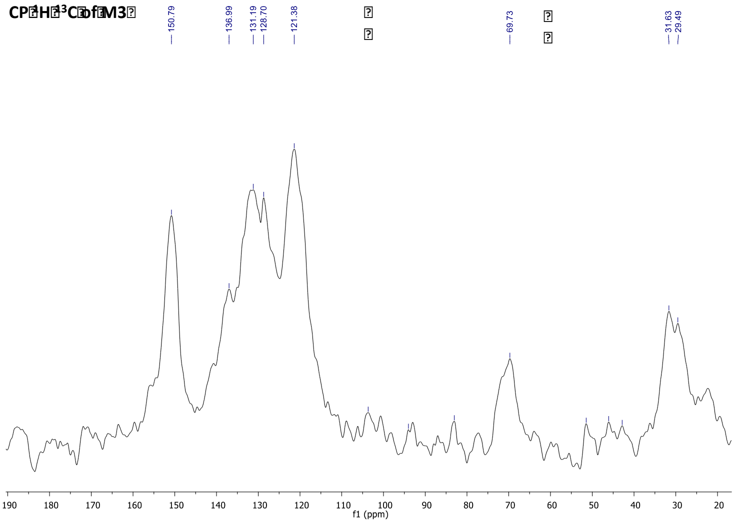
[1] N. Launay, A. M. Caminade, R. Lahana, J. P. Majoral, *Angew. Chem. Int. Ed. Engl,.* 1994, 33, 1589-1592.

Figure S2. Typical CP ^{13}C and CP ^{31}P MAS NMR.

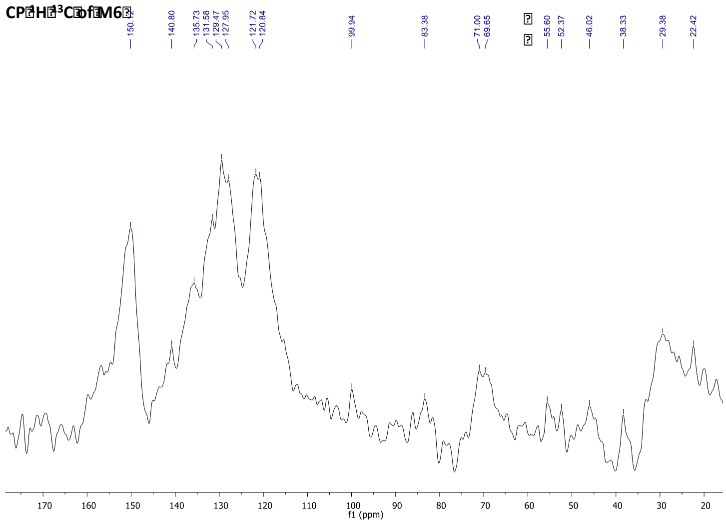
CP ^{1}H ^{13}C of M1



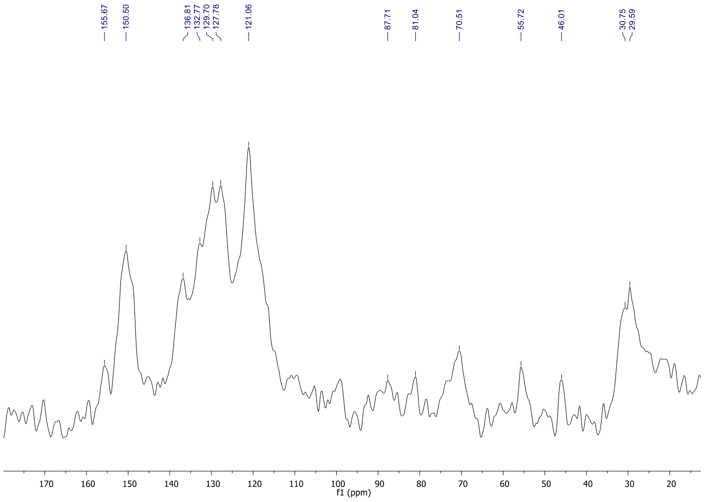
CP ^{1}H ^{13}C of M3



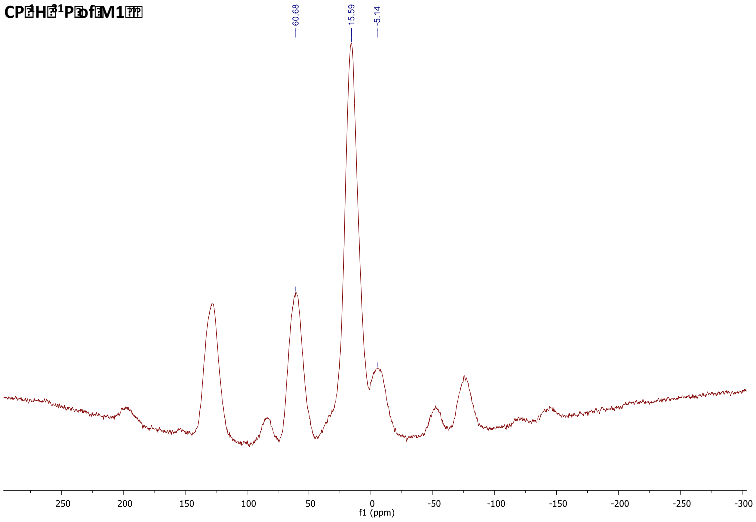
CP ^{1}H ^{13}C of M6



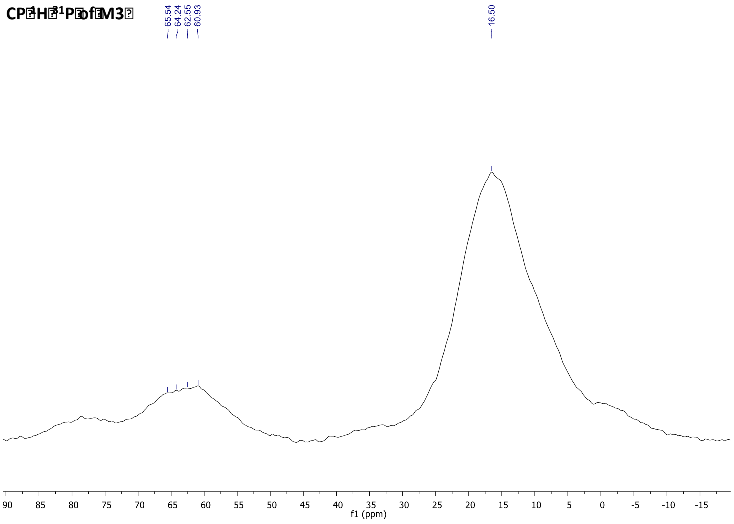
CP ^{1}H ^{13}C of M7

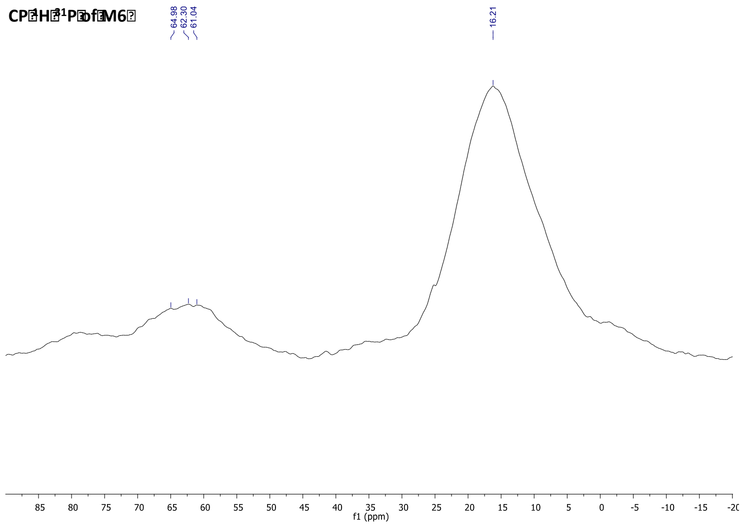


CP ^{1}H ^{31}P of M1



CP ^{1}H ^{31}P of M3





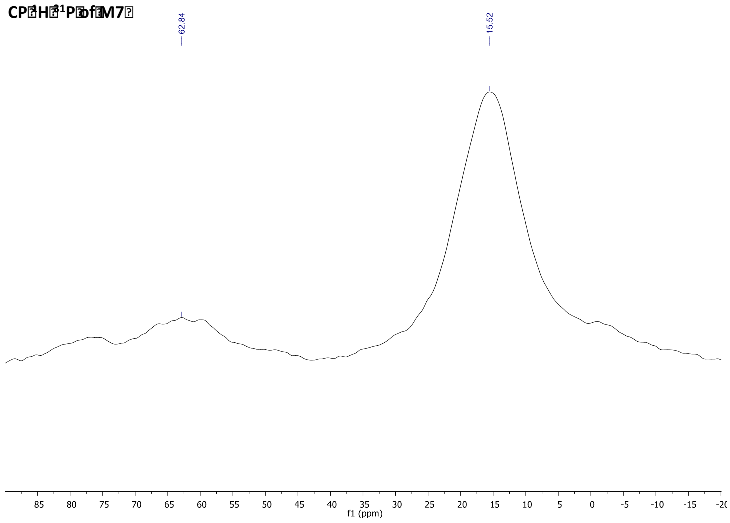


Figure S3. Typical X-ray diffraction of the as-synthesized hybrid material at 60°C.

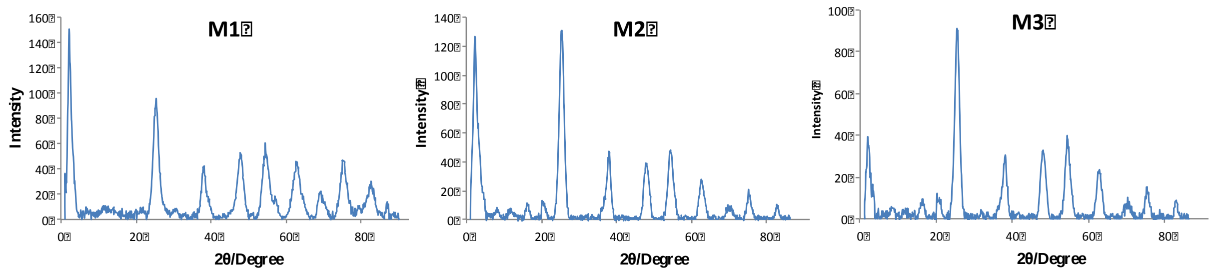
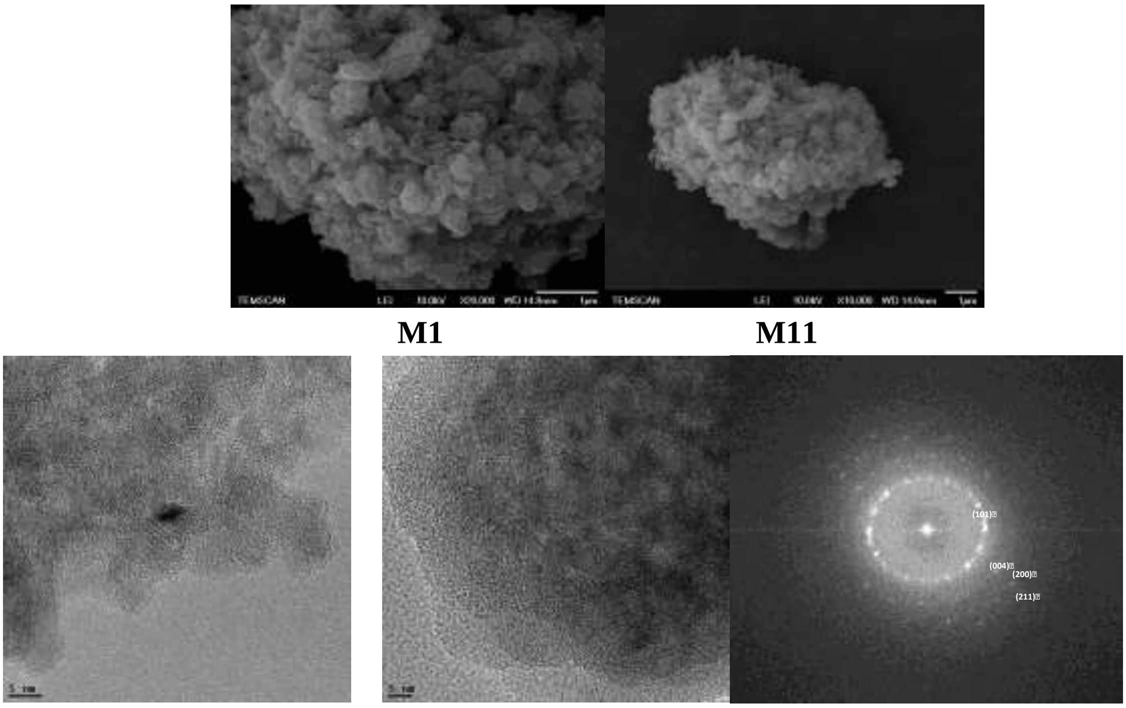


Figure S4. Selected SEM, HRTEM and SAED of the as-synthesized hybrid materials.



M1 **M11**

M1 **M3** **M1**

Figure S5. Nitrogen sorption analysis.

Figure S5a. Influence of the dendrimer generation

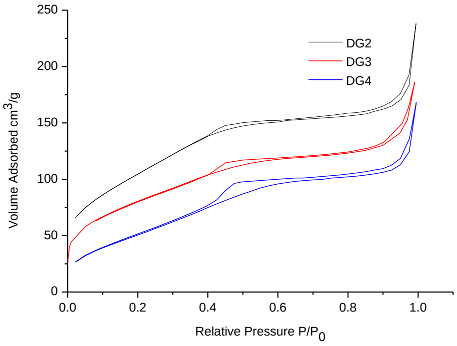
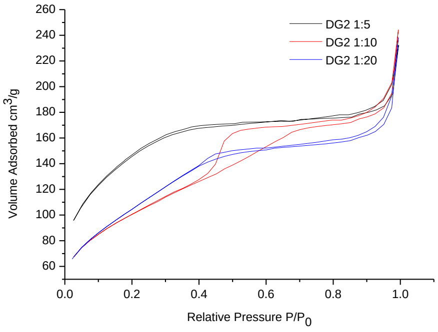


Figure S5b. Influence of the dendrimer: titanium alkoxide ratio

Titanium alkoxide	Phosphonate[a]	Ratio (P:Ti)	Solvent	T (°C)	S_{BET}[b] (m^2.g^{-1})	Size[c] (nm)
Ti(OiPr)$_4$	DG$_2$	1 :5	EtOH	60	511	6
Ti(OiPr)$_4$	DG$_2$	1 :10	EtOH	60	356	5.9
Ti(OiPr)$_4$	DG$_2$	1 :20	EtOH	60	386	6
Ti(OiPr)$_4$	DG$_3$	1 :5	EtOH	60	514	5.5
Ti(O*i*Pr)$_4$	DG$_3$	1 :10	EtOH	60	289	5.7
Ti(OiPr)$_4$	DG$_3$	1 :20	EtOH	60	291	5.8

[a] The organo-terminated phosphonate additives introduced in the medium. **DG$_3$** and **DG$_2$** are respectively the third and second generation phosphonate-terminated dendrimers ((P(O)(OH)(O$^-$Na$^+$)). [b] Specific surface areas of the as-synthesized hybrid materials as determined by nitrogen sorption analysis. [c] The particle size of the crystalline anatase calculated from X-ray diffraction analysis.



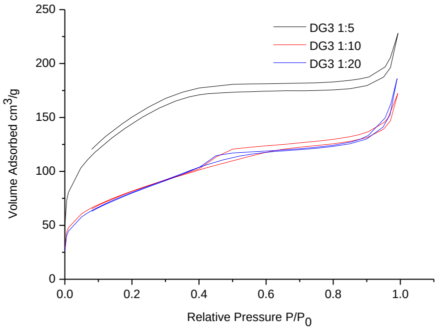


Figure S5c. Influence of the monomer hydrolysis-condensation kinetics

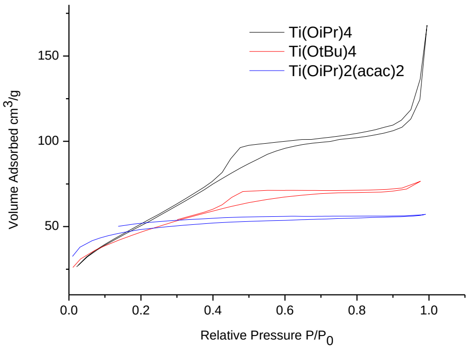


Figure S5d. Influence of the Temperature (T = 25°C, 60°C and 100°C)

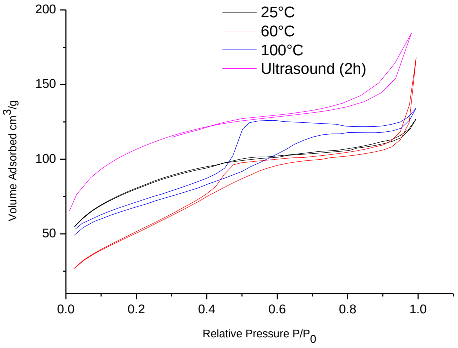


Figure S5e. Solvent effect

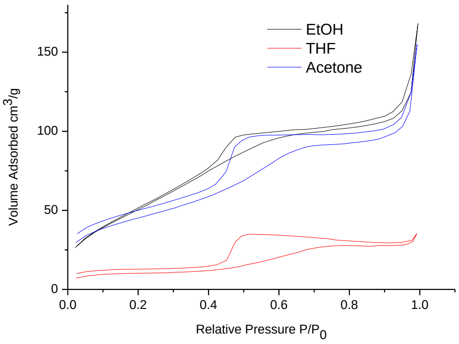


Figure S6. TGA analysis of the hybrid materials as a function of dendrimer:titanium alkoxide ratio.

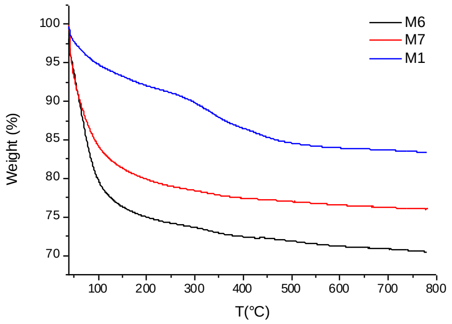


Figure S7. TGA analysis of the hybrid materials as a function of the monomer hydrolysis.

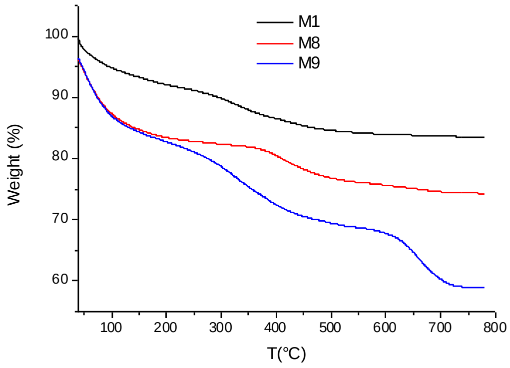


Figure S8. TGA analysis of the hybrid materials as a function of the temperature.

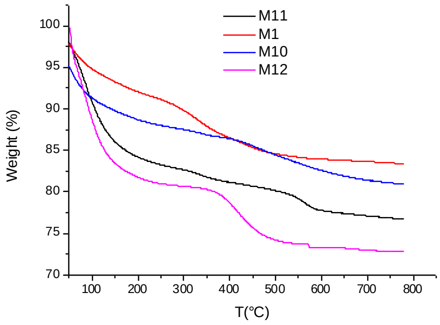


Figure S9. TGA analysis of the hybrid materials as a function of the solvent.

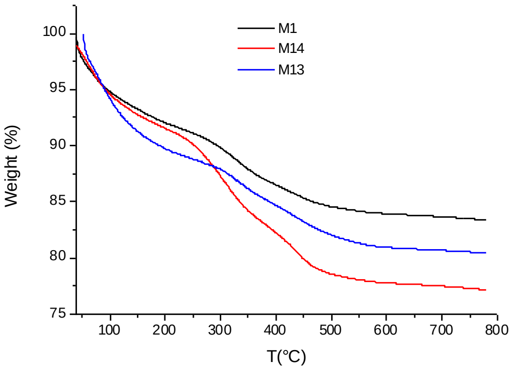


Figure S10. RAMAN spectroscopic studies of M4 and M9.

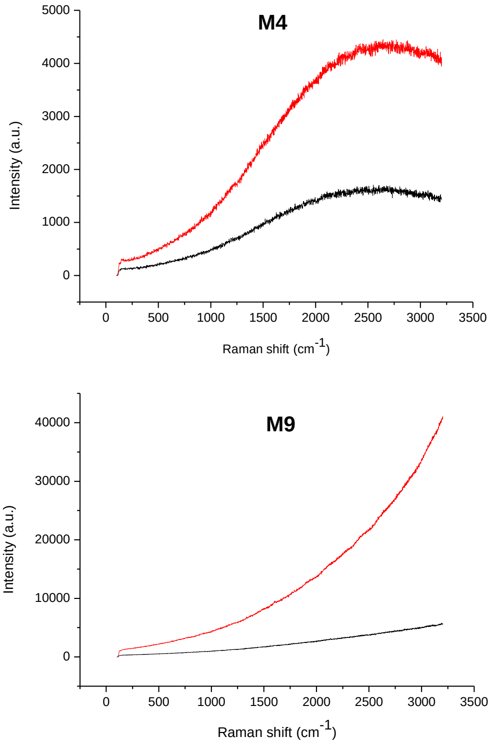


Figure S11. X-ray diffraction of the thermally annealed material M1 at various temperatures.

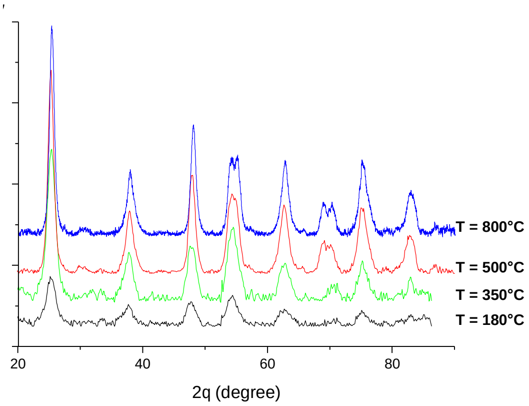
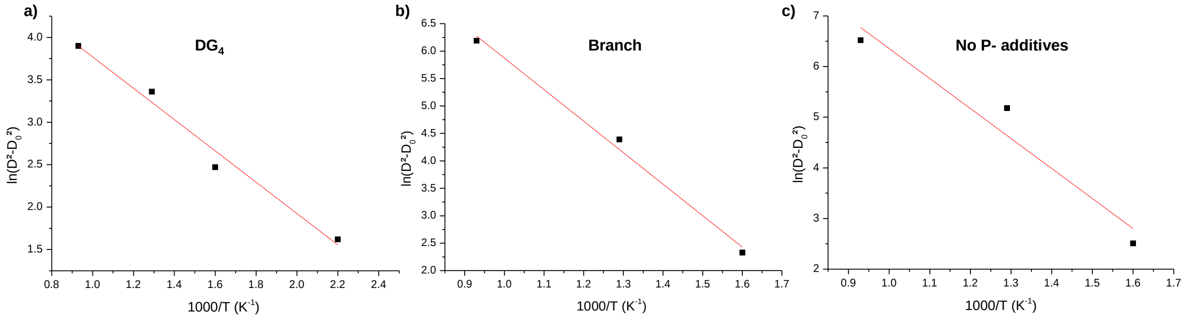


Figure S12. Determination of the activation energy for crystal grain growth according to Eq. 1.



Sol-gel standard mineralization of Ti(O*i*Pr)$_4$ performed in ethanol-water mixture at 60°C in presence of a) the fourth generation phosphonate-terminated dendrimers (case of **M$_1$**), b) in presence of the branch-mimicking dendrimers (case of **M$_4$**) and c) in the absence of any phosphorus additive (case of **M$_5$**).