PAPER www.rsc.org/obc | Organic & Biomolecular Chemistry

Synthesis and characterization of photoluminescent vinylbiphenyl decorated polyhedral oligomeric silsesquioxanes†‡

Nicolas R. Vautravers,[a] Pascal André,*[b] A. M. Z. Slawin[a] and David J. Cole-Hamilton*[a]

Received 20th August 2008, Accepted 4th November 2008
First published as an Advance Article on the web 11th December 2008
DOI: 10.1039/b814496f

Grubbs cross-metathesis has been used to functionalize octavinylsilsesquioxane with fluorescent vinylbiphenyl-modified chromophores to design new hybrid organic-inorganic nanomaterials. Those macromolecules have been characterized by NMR, microanalyses, MALDI-TOF mass spectrometry and photoluminescence. This last method was shown to be an interesting tool in the analysis of the purity of the cube derivatives.

Introduction

Dendrimers are tree-like, highly branched, monodisperse macromolecules composed of a central core, branches comprising repeated branching units radiating from it, and surface groups located on the exterior of the dendrimer providing further functionality. They offer numerous interesting properties resulting from the globular shape they often adopt at high generation, so the range of their applications spans through drug delivery systems,[1] molecular recognition,[2–5] catalysis supports,[6–9] magnetic resonance imaging contrast agents,[10] DNA intercalation compounds[11] and light-emitting materials.[12,13]

Among these dendrimers, cubic polyhedral oligomeric silsesquioxanes (POSSs) of chemical formula $R_8Si_8O_{12}$, with R groups at the vertices of a cube and bridged by oxygen atoms, are of special interest because of their nanometre-size allowing the use of silicon atoms for the design of multifunctional molecules. They have been mainly employed in materials chemistry ranging from models of silica surface [14] and zeolites [15] to organic-inorganic hybrid polymers.[16] POSS-chromophore hybrid molecules have also attracted interest, among other reasons, because of their better casting and layer-forming properties than those of pure chromophores, especially in the context of applications including organic semiconductors and solution processable light-emitting diodes.[17–19] Additionally, the attachment of luminescent chromophores to the rigid POSS core is of scientific interest with regard to its effect on fluorescence quantum yield as well as for the design of multifunctional colloidal molecules.[20,21] A key issue for these potential applications of silsesquioxanes is their relative ease of synthesis in multigram quantities, avoiding acidic [22] or basic conditions[23,24] which might disrupt the POSS core. Recent advances have seen many new POSS species prepared by cross-metathesis,[17,25,26] hydrosilylation[27,28] or hydrolysis of $RSiY_3$.[29] We previously reported on the successful elaboration of a variety of new functionalisable dendrimer cores based on octavinylsilsesquioxane[20,30] and wish further to extend our studies in this paper. We expand the library of organic-inorganic hybrid-decorated polyhedral oligomeric silsesquioxanes by presenting the synthesis of a new family of photoluminescent vinylbiphenyl-terminated POSS-cored dendrimers together with their optical characterization. While trying to gain deeper insight into the effect of these chromophore-grafted rigid POSSs on fluorescence quantum yield, we show that the photoluminescent properties of these organic-inorganic hybrid macromolecules demonstrate some limitations of traditional characterisation techniques for the identification of minor side products.

Results and discussion

Three macromolecules (**S**) have been prepared *via* Grubbs metathesis between the readily available octavinylsilsesquioxane and a vinylbiphenyl-decorated monomer (**M**) (Scheme 1). During the Grubbs coupling, the homometathesis side product (**H**) from **M** was always produced together with the macromolecule and ethene. The reaction system is even more complex, as the olefin metathesis is reversible (equilibrium); in the given case, the removal of ethene assures complete conversion from octavinylsilsesquioxane + **M** to **S** + **H**. The cross-metathesis between two POSS species has never been observed, probably for steric reasons.

The vinyl biphenyl group was selected because of its versatile chemistry and strong photoluminescence properties. The chemical functionalising groups R were chosen for their abilities to further elaborate on xxthe resulting compound structure and properties by simple chemistry. In this context, three **M** monomers were synthesised *via* Suzuki coupling between styreneboronic acid and the desired haloaromatic compound. This yielded chromophores with a vinylbiphenyl backbone decorated with one methylenedioxy group **M1**, two methoxy groups **M2** or two methyl dicarboxylate

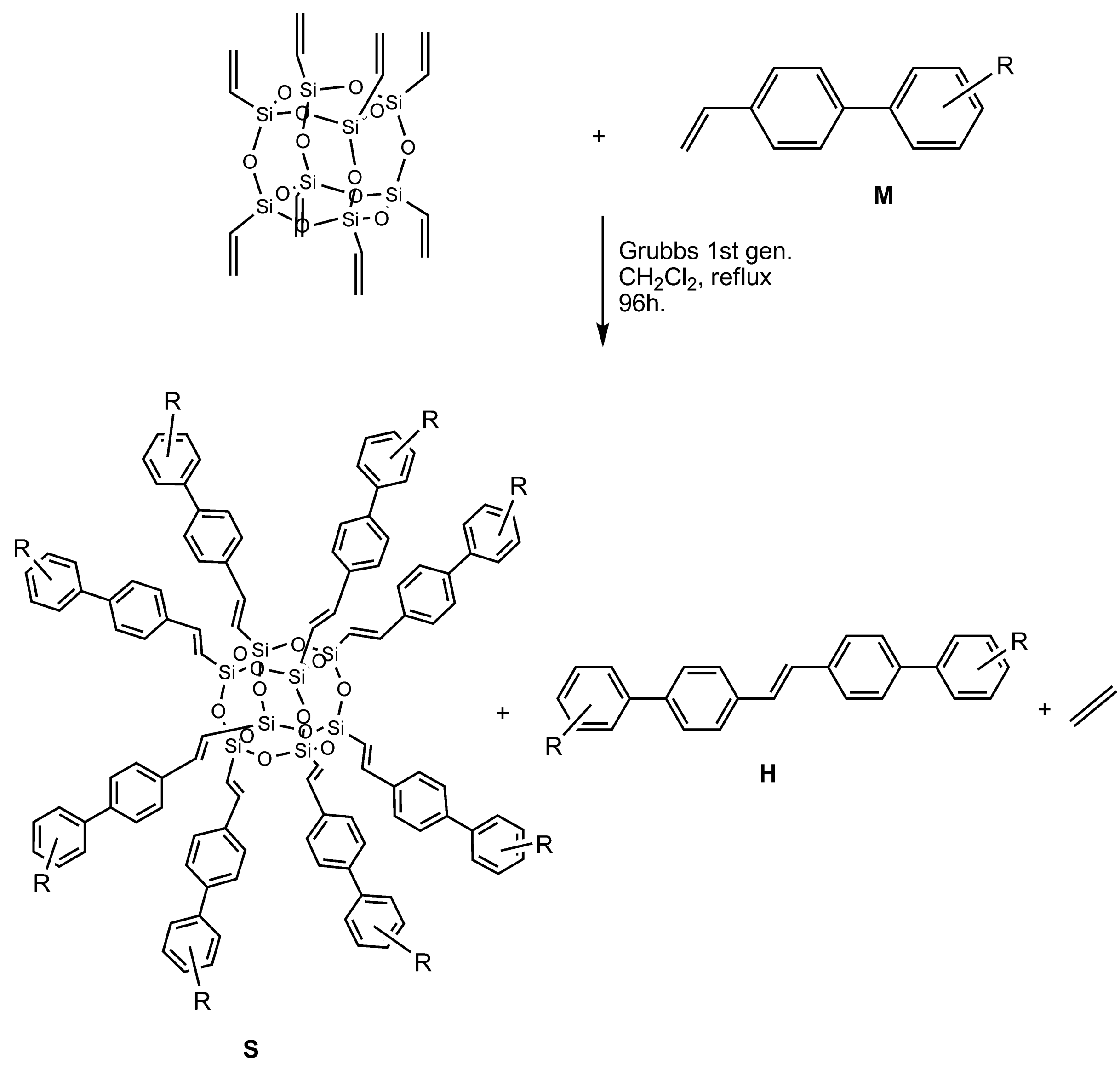
---

[a] *EaStCHEM, School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, UK. E-mail: djc@st-and.ac.uk; Fax: +44-1334-463808; Tel: +44-1334-463805*

[b] *Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St Andrews, St Andrews, Fife, Scotland, KY16 9SS, UK. E-mail: pa11@st-and.ac.uk*

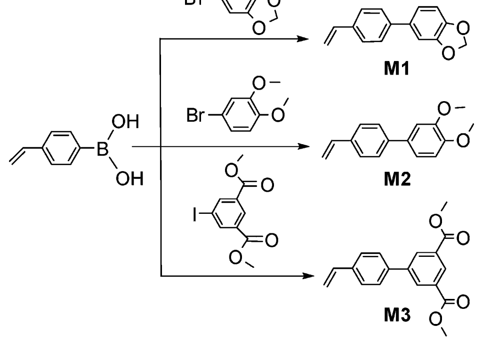
† Electronic supplementary information (ESI) available: Crystal structure of **H3**. CCDC reference number ??. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814496f

‡ $C_{34}H_{28}O_8$, $M = 564.56$, monoclinic, space group $P2_1/c$, $a = 4.7172(6)$ $b = 14.805(2)$, $c = 19.787(3)$ Å, $\beta = 93.810(4)°$ $U = 1378.8(3)$ Å^3, $Z = 2$, $D_c = 1.360$ Mg m^{-3}, $\mu = 0.097$ mm^{-1}(Mo-Kα, $\lambda = 0.71073$ Å). The data were collected at $T = 93(2)$ K, 8788 reflections were measured on a Rigaku MM007RA/Confocal Optics/Mercury CCD diffractometer equipped with an Xstream low-temperature device yielding 2459 unique data ($R_{merg} = 0.0307$). Conventional $R = 0.0432$ for 2121 reflections with $I \geq 2\sigma$, GOF = 1.051. Final $wR2 = 0.1201$ for all data. The largest peak in the residual map is 0.203 e Å^{-3}.



Scheme 1 Synthetic pathway of macromolecule (**S**) and homo-Grubbs side product (**H**) from vinylbiphenyl monomer (**M**) and octavinylsilsequioxane.

groups **M3** (Scheme 2). The two first monomers **M1** and **M2** can lead, after deprotection, to diol-decorated biphenyls which allow subsequent functionalization through a variety of reactions such as transesterification or nucleophilic substitution,[31] whilst dimethyl ester groups present on **M3** are interesting candidates for polymerisation.



Scheme 2 Formation of monomer (**M**) *via* Suzuki coupling between styreneboronic acid and the desired haloaromatic compound.

The photophysical properties and mass characterisation of these three compounds were then investigated through a combination of absorbance (Abs), photoluminescence (PL), photoluminescence excitation (PLE) measurements and High Resolution Mass Spectrometry (HRMS) as reported in Fig. 1 and Table 1; see experimental for details.

The photophysical properties of the three monomers are fairly consistent with those of vinylbiphenyl which is characterised in THF by absorption and photoluminescence peaks at 278 nm and 317 nm, respectively,[20,32] while the observed shifts result from the slight perturbation of the electronic properties induced by the functional groups; see Table 1. The PLQY variation observed between each monomer can be rationalised by the degree of freedom, *i.e.* rotational and vibrational, associated

Table 1 Absorbance peak, position of the first photoluminescence peak, photoluminescence quantum yield (PLQY) measured at the indicated wavelength and high resolution mass spectroscopy (HRMS)

Structure	**M1**	**M2**	**M3**
Abs. peak (nm)	301	300	280
1st PL peak (nm)	374	374	355
PLQY (%)	40 @ 300 nm	60 @ 300 nm	14 @ 280 nm
HRMS (g/mol)	225.0921, requires 225.0911	263.1046, requires 263.1048	297.1129, requires 297.1127

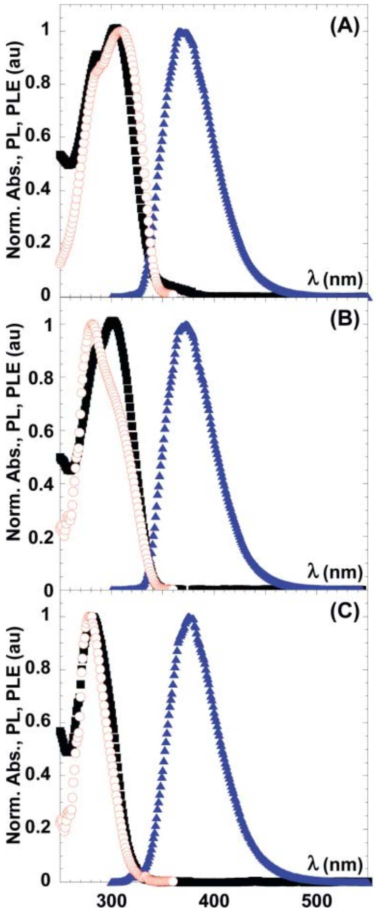


Fig. 1 Normalized absorbance (Abs., ■), photoluminescence (PL, ▲, λ_{exc}: 290 nm) and photoluminescence excitation (PLE, ○, λ_{detec}: 340 nm) spectra associated with the monomers **M1** (A), **M2** (B) and **M3** (C).

with the external functional groups as would be expected in rigidochromic systems.[33,34] For instance, the methoxy groups of **M2** induce an increase of the PLQY when compared to the pure vinylbiphenyl chromophore, 60% and 45% respectively, whereas the PLQY decreases dramatically passing from the rigid diol-protected monomers **M1** and **M2** to the more flexible ester **M3**.

For each monomer, the close match between the PLE spectrum and the absorbance testifies to the high purity of the prepared compounds, further confirmed by mass spectrometry (Table 1).

Monomers (**M**) were then coupled to octavinylsilsesquioxane *via* a Grubbs-type reaction, affording the corresponding macromolecules (**S**) (Fig. 2). After precipitation in a mixture of ethyl acetate (120 mL) and petroleum ether (40–60) (500 mL), the three macromolecules were subjected to column chromatography, and their purity was attested on the one hand by both microanalysis and MALDI mass spectroscopy (Table 2) and on the other hand by the cross-peaks that appear on their ^{29}Si^{1}H HMQC 2D NMR spectrum, illustrated in Fig. 3 for the macromolecule **S2**. The cross-peaks correspond to the clean coupling between a corner silicon atom and the alkenyl protons at 6.49 ppm and 7.51 ppm. The sharp cross-peaks indicate that the cube is intact and unique and that each corner is equivalent. Similar observations have been made for the other three macromolecules, highlighting the uniqueness of each cube.

The optical characterisation and mass characterisation of the macromolecules is reported in Fig. 4 and Table 2. Due to a more extensive electron delocalisation into the POSS core, grafting **M** monomers onto the POSS cube leads to the expected slight red shift in the absorbance and PL spectra compared to the free dendrons.[20,32] Broader PL spectra are also observed for the three **S** macromolecules as more conformations become accessible to the chromophores.[35] The side products give rise to absorption features at *ca.* 345 nm, confirmed by extra peaks in this region in the PLE spectrum. These photophysical methods seem to provide the only analytical technique that reveals the presence of this side product. In the case of **S1** and **S2**, the side-products precipitated as powders during the course of the Grubbs coupling and were isolated by filtration, whilst silica gel column chromatography was performed for **S3**, as both product and side product were soluble in the reaction mixture.

The **H** side products were identified by HRMS as arising from self-metathesis of the **M** monomers (Table 3 and Fig. 5). In the mixtures **S1** + **H1** and **S2** + **H2**, the grafted **M** segments possess low solubility in apolar solvents, not much enhanced by the substituents R; see Scheme 1. In the POSS compounds **S**, the grafted **M** segments have worse possibilities for higher regular

Table 2 Absorbance peak, position of the first photoluminescence peak, photoluminescence quantum yield (PLQY) measured at the indicated wavelength and matrix-assisted laser desorption/ionization (MALDI) mass spectroscopy

Structure	**S1**	**S2**	**S3**
Abs. peak (nm)	311	310	285
1st PL peak (nm)	382	380	375
PLQY (%)	<50 @ 300 nm	<55 @ 300 nm	<11 @ 290 nm
MALDI (g/mol)	2202.44, requires 2201.84	2330.30, requires 2329.92	2802.41, requires 2801.08

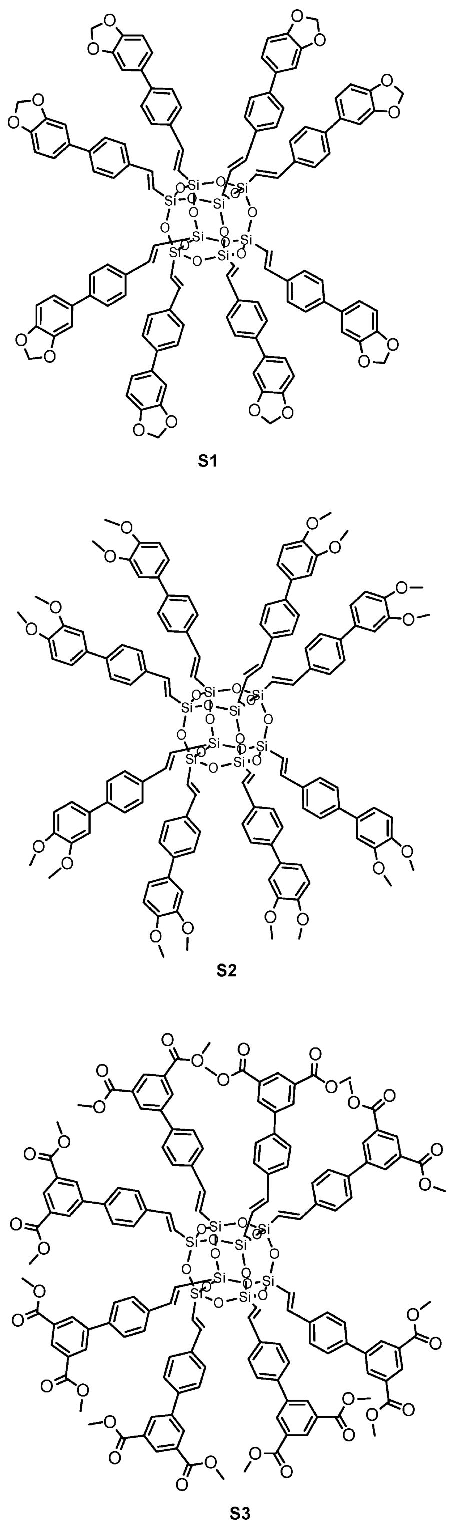


Fig. 2 Representation of macromolecules **S1**, **S2** and **S3**.

crystallization than in the **H** products, which are hence less soluble and precipitate more easily. In the case of **S3**, this effect is cancelled by the high solubility of the **M** segments given by the ester groups on them; see Scheme 2. The chromatographic behavior of both **S3** and **H3** is thus dominated by mutual affinity and similar high solubility making their separation more complex.

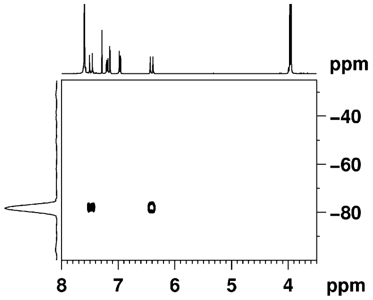


Fig. 3 ^{29}Si^{1}H HMQC 2D NMR of **S2**.

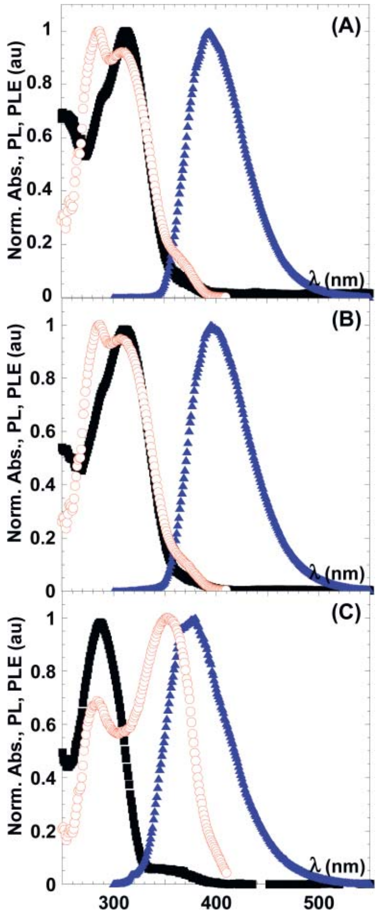


Fig. 4 Normalized Abs. (■), PL (▲, λ_{exc}: 290 nm) and PLE (○, λ_{detec}: 420 nm) spectra associated with the macromolecules **S1** (A), **S2** (B) and **S3** (C).

H3 with substituent MeO$_2$C- groups was characterised crystallographically‡. The X-ray structure of **H3** reveals that the molecule is planar, has an *E* double bond and is disposed about a centre of symmetry at the middle of the double bond. The central bond length is 1.330(3) Å. The terminal aryl rings are inclined by 26° with respect to the central aryl rings whilst the ester substituents are essentially coplanar with the terminal aryl rings.

The photophysical properties of these homo-metathesis products are shown in Fig. 6 and Table 3. As a result of the increase in the conjugation length associated with the dimerisation, the expected red shift of both the absorption and PL features for the three homo-metathesis products compared with the free

Table 3 Absorbance peak, position of the first photoluminescence peak, photoluminescence quantum yield (PLQY) measured at the absorbance maximum and high resolution mass spectroscopy (HRMS)

Structure	**H1**	**H2**	**H3**
Abs. peak (nm)	350	350	345
1st PL peak (nm)	402	400	390
PLQY (%)	66 @ 350 nm	80 @ 350 nm	70 @ 350 nm
HRMS (g/mol)	421.1436, requires 421.1440	453.2061, requires 453.2066	565.1864, requires 565.1860

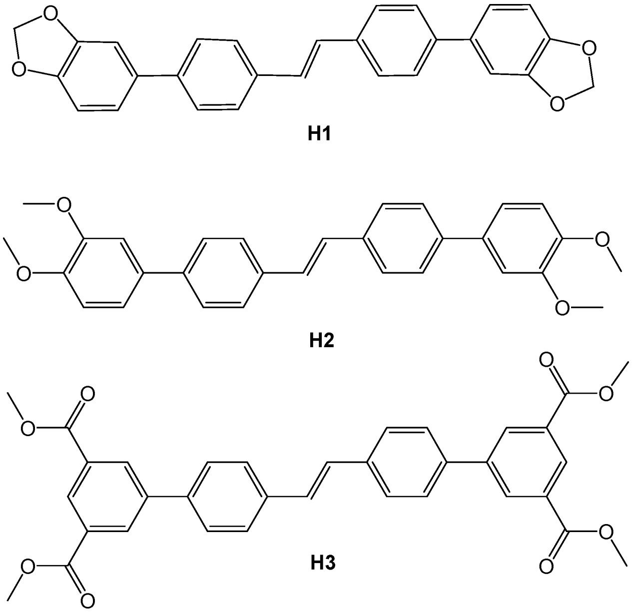


Fig. 5 Representation of homo-metathesis products **H1**, **H2** and **H3**‡.

momomers is observed; see Table 2 and Table 3. The PL spectra of the homo-metathesis products display similar substructures, although they are shifted slightly because of the different effects of the aromatic substituents. For all three **H** chromophores, the PLQY is much higher than for **M** and **S** molecules, being up to 80% for **H2**, consistent with the rigidochromy already mentioned for the monomers. In addition, absorption and PLE spectra match one another and the maxima correspond exactly to the side products identified during the photophysical studies of the **S** macromolecules.

In this context, the high PLQYs of these dimers explain why the relatively small amount of homo-metathesis product remaining after purification of the macromolecules would lead to an overestimation of the PLQY of the macromolecules. The higher intensity of the photoluminescence from the side product observed in the PLE for **S3** (see Fig. 6C) can now be explained: **H3** has been isolated chromatographically, but its similar polarity or intercalation within the macromolecule makes complete separation from the macromolecule difficult, even after several cycles. Conversely, the precipitation of **H1** and **H2** in the course of the Grubbs reaction, followed by their filtration, allows for better purification.

The PLQY of all the compounds synthesized and characterised in the present work are compared in Table 1, Table 2 and Table 3. On the basis of simple considerations of translational, vibrational and rotational degrees of freedom, **M3**, **S3** and **H3** should, and do (at least in the cases of **M1** and **S1**) exhibit the lowest PLQY. Rather unexpectedly, the PLQYs for **M2**, **S2** and **H2** are higher than those for **M1**, **S1** and **H1**. The origin of this effect is not clear.

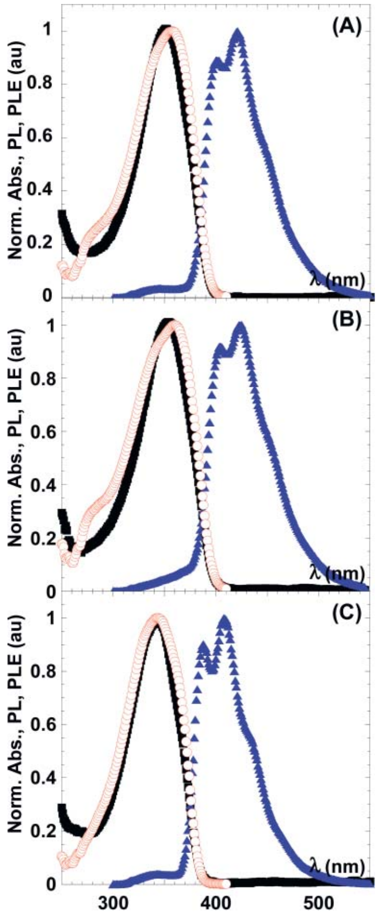


Fig. 6 Normalized Abs. (■), PL, (▲, λ_{exc}: 290 nm) and PLE (○, λ_{detec}: 420 nm) spectra associated with the homo-metathesis products **H1** (A), **H2** (B) and **H3** (C).

While targeting specific applications in the biomedical and material fields, it is crucial to select the appropriate synthetic pathways to control the exact composition of the final product without inducing side effects or altering the thermal/mechanical/electrical material properties. In this context it is then worth noting that the presence of the homo-metathesis product within the final product has only been identified through its photophysical properties. None of NMR, MALDI-TOF or microanalysis were able to distinguish between the small molecule and the macromolecule.

Conclusions

We have shown the synthesis and characterization of three new light-emitting macromolecules based on vinylbiphenyl decorated polyhedral oligomeric silsesquioxanes. They have been characterized by NMR, microanalysis and MALDI-TOF spectroscopy. Optical measurements were shown to be an interesting and crucial tool in analyzing the purity of these compounds.

Experimental

All manipulations were carried out under dry, deoxygenated (Cr^{II} on silica) nitrogen using standard Schlenk techniques. Before use, solvents were degassed and dried by distillation from sodium diphenyl ketyl (THF) or calcium hydride (CH_2Cl_2). Water was distilled and stored under nitrogen. 4-bromo-1,2-(methylenedioxy)benzene, 4-bromo-1,2-dimethoxybenzene, 4-styrene boronic acid, $[Pd(PPh_3)_4]$, $[Ru(=CHPh)Cl_2(PCy_3)_2]$ (Grubbs' catalyst, 1st gen.) and lithium 2,4-pentanedioate were purchased from Aldrich and used without further purification.

Microanalyses were carried out on a Carlo Erba 1110 CHNS analyser. A Micromass GCT provided Chemical Ionisation (CI) at low and high resolution and a Micromass LCT provided a low and high resolution Electrospray Ionisation Service (ESI). NMR spectra were recorded on a Bruker Avance 300 or a Bruker Avance II 400 NMR spectrometer. The ^1H, ^{13}C and ^{29}Si NMR spectra were recorded with reference to tetramethylsilane. ^{31}P NMR spectra were referenced externally to 85% H_3PO_4. Matrix-assisted laser desorption/ionization (MALDI) mass spectra were obtained using a Micromass TOF Spec 2E mass spectrometer system equipped with a 337 nm N_2 laser operating in the positive ion detection mode. Samples were generated by adding NaI to the matrix (α-cyano-4-hydroxycinnamic acid or 2,5-dihydroxybenzoic acid, as an ionization promoter) and dissolved in a suitable solvent (THF or CH_2Cl_2) before being transferred to the sample holder and dried. The spectra were calibrated using a tryptic digest of the β-galactosidase protein.

Data for **H3** were corrected for Lorentz, polarization and absorption effects. The structures were solved by direct methods and refined by full-matrix least squares on xxF^2 for all data using SHELXTL software. The non-hydrogen atoms were refined with anisotropic thermal parameters and C–H hydrogen atoms were assigned riding isotropic thermal parameters and constrained to idealised geometries.

Absorption spectra were recorded using a Cary 300 spectrophotometer, 10 mm optical path fluorescence cuvettes (Hellma) and the concentration was adjusted to reach an optical density of about 0.1. Photoluminescence (PL) spectra were recorded with a Jobin Yvon Horiba Fluoromax 2 fluorimeter. Spectra were corrected for grating and detector sensitivity variation with wavelength. Except when stated otherwise, all the photophysical properties were characterised at room temperature and in non degassed THF solution. The photoluminescence quantum yields (PLQY) were measured against quinine sulfate (Fluka) in 0.5 M sulfuric acid (Sigma-Aldrich) solution used as a standard because of its known quantum yield of 54.6% as well as its very small sensitivity to oxygen quenching. PLQY falls down to 45% in non degassed THF. The following equation was used to perform the appropriate corrections:[36]

$$\Phi_x = \Phi_r \left(\frac{A_r(\lambda_r)}{A_x(\lambda_x)}\right)\left(\frac{I(\lambda_r)}{I(\lambda_x)}\right)\left(\frac{n_x}{n_r}\right)^2\left(\frac{D_x}{D_r}\right)$$

where Φ stands for PLQY, the subscripts x and r refer to the compound to be characterized and to the reference solutions, respectively. λ is the excitation wavelength, $A(\lambda)$ is the absorbance, $I(\lambda)$ is the relative intensity of the exciting light, n is the solvent refractive index, and D is the integrated area under the corrected emission spectrum.

4-Styryl-1,2-(methylenedioxy)benzene (M1)

A mixture of 4-bromo-1,2-(methylenedioxy)benzene (1.3 mL, 10.8 mmol), 4-styrene boronic acid (2 g, 13.5 mmol), $[Pd(PPh_3)_4]$ (374 mg, 0.32 mmol), K_2CO_3 (2M, 37.8 mmol) and THF (70 mL) was heated at 75 °C for 48 hours. After cooling to room temperature, CH_2Cl_2 (50 mL) and water (20 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$. After evaporation of the solvents, flash column chromatography with CH_2Cl_2 afforded **M1** as a white luminescent powder (2.38 g, 98%) (Found: C, 80.0; H, 5.2. $C_{15}H_{12}O_2$ requires C, 80.4; H 5.4%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 5.27 (1 H, d, $^3J_{HH}$ 11.6, CH_2=CH), 5.79 (1 H, d, $^3J_{HH}$ 18.3, CH_2=CH), 6.01 (2 H, s, OCH_2O), 6.76 (1 H, dd, $^3J_{HH}$ 11.6 Hz, $^3J_{HH}$ 18.3, CH_2=CH), 6.90 (1 H, m), 7.09 (2 H, m) and 7.49 (4 H, m); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 101.6 (OCH_2O), 107.9, 109.0, 114.2 (CH_2=CH), 120.9, 127.3, 127.4, 135.5, 136.7, 136.8, 140.7, 147.5 and 148.8; m/z (CI) 225.25 (M+1. $C_{15}H_{13}O_2$ requires 225.26).

1,3,5,7,9,11,13,15-Octakis[2-ethenyl]pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (S1)

An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under nitrogen with octavinylsilsesquioxane[37] (100 mg, 0.16 mmol) and 4-styryl-1,2-(methylenedioxy)benzene **M1** (624 mg, 2.78 mmol) in CH_2Cl_2 (10 mL). The solution of Grubbs′ catalyst (5 mg, 0.006 mmol) in CH_2Cl_2 (3 mL) was injected in the mixture heated at 55 °C to maintain a gentle reflux. The reaction was stopped and cooled to room temperature after disappearance of the vinyl signals in the ^1H NMR spectrum (90 hours). The mixture was filtered (isolation of **H1**), concentrated and precipitated by adding the crude product in CH_2Cl_2 to a solution of ethyl acetate (120 mL) and petroleum ether (40–60) (500 mL). The residue was loaded onto a silica gel column and eluted with CH_2Cl_2 affording **S1** as a white powder (231 mg, 67%) (Found: C, 65.2; H, 4.0. $C_{120}H_{88}O_{28}Si_8$ requires C, 65.5; H, 4.0%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 6.01 (16 H, s, OCH_2O), 6.37 (8 H, d, $^3J_{HH}$ 18.6, SiCH=CH), 6.90 (8 H, m), 7.09 (16 H, m), 7.44 (8 H, d, $^3J_{HH}$ 18.6, SiCH=CH) and 7.54 (32 H, m); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 101.6 (OCH_2O), 108.0, 109.0, 117.0 (SiCH=CH), 120.9, 127.3, 127.4, 135.5, 136.7, 140.7, 147.6, 148.5 (SiCH=CH) and 149.0; δ_{Si}(79.5 MHz; $CDCl_3$; Me_4Si) −77.6 (O_3Si); m/z (MALDI) 2202.44 (M. $C_{120}H_{88}O_{28}Si_8$ requires 2201.84).

(**H1**) (282 mg, 69% based on unreacted **M1**); m/z (CI) 421.1436 (M+1. $C_{28}O_4H_{21}$ requires 421.1440).

3,4-Dimethoxy-4′-vinylbiphenyl (M2)

A mixture of 4-bromo-1,2-dimethoxybenzene (2.3 mL, 16.0 mmol), 4-styrene boronic acid (3 g, 20.3 mmol), $[Pd(PPh_3)_4]$ (562 mg, 0.48 mmol), K_2CO_3 (2M, 56.8 mmol) and THF (70 mL) was heated at 75 °C for 48 hours. After cooling to room temperature, CH_2Cl_2 (50 mL) and water (20 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$. After evaporation of the solvents, flash column chromatography with CH_2Cl_2 afforded **M2** as a white luminescent powder (2.05 g, 53%) (Found: C, 79.6; H, 6.9. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%); δ_H(300.13 MHz; $(CD_3)_2SO$; Me_4Si) 3.79 (3 H, s, OCH_3), 3.85 (3 H, s, OCH_3), 5.28 (1 H, d, $^3J_{HH}$ 11.1, CH_2=CH), 5.87 (1 H, d, $^3J_{HH}$ 17.8, CH_2=CH), 6.77 (1 H, dd, $^3J_{HH}$ 11.1, $^3J_{HH}$ 17.8, CH_2=CH), 7.03 (1 H, d, $^3J_{HH}$ 8.3), 7.22 (1 H, d, $^3J_{HH}$ 8.3), 7.23 (1 H, s), 7.53 (2 H, d, $^3J_{HH}$ 8.2) and 7.65 (2 H, d, $^3J_{HH}$ 8.2); δ_C (75.5 MHz; $(CD_3)_2SO$; Me_4Si) 55.5 (OCH_3), 110.2, 112.1, 114.0 (CH_2=CH), 118.7, 126.4, 126.6, 132.3, 135.6, 136.2, 139.5, 148.6 and 149.0; *m/z* (ESI) 263.1046 (M+Na. $C_{16}H_{16}O_2Na$ requires 263.1048).

1,3,5,7,9,11,13,15-Octakis[2-ethenyl]pentacyclo [9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (S2)

An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under nitrogen with octavinylsilsesquioxane[37] (100 mg, 0.16 mmol) and 3,4-dimethoxy-4′-vinybiphenyl **M2** (662 mg, 2.76 mmol) in CH_2Cl_2 (10 mL). The solution of Grubbs′ catalyst (5 mg, 0.006 mmol) in CH_2Cl_2 (3 mL) was injected in the mixture heated at 55 °C to maintain a gentle reflux. The reaction was stopped and cooled down to room temperature after disappearance of the vinyl signals in the ^{1}H NMR spectrum (90 hours). The mixture was filtered (isolation of **H2**), concentrated and precipitated by adding the crude product in CH_2Cl_2 to a solution of ethyl acetate (120 mL) and petroleum ether (40–60) (500 mL). The residue was loaded onto a silica gel column and eluted with a gradient of CH_2Cl_2 and $(CH_3)_2CO$ (CH_2Cl_2 → $(CH_3)_2CO$) affording **S2** as a white powder (252 mg, 69%) (Found: C, 65.3; H, 4.8. $C_{128}H_{120}Si_8O_{28}$ requires C, 65.9; H, 5.2%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 3.93 (24 H, s, OCH_3), 3.96 (24 H, s, OCH_3), 6.39 (8 H, d, $^3J_{HH}$ = 19.2, SiCH=CH), 6.95 (8 H, d, $^3J_{HH}$ 8.68), 7.16 (16 H, m), 7.46 (8 H, d, $^3J_{HH}$ 19.2, SiCH=CH) and 7.58 (32 H, m); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 56.0 (OCH_3), 110.3, 111.5, 117.2 (SiCH=CH), 119.4, 127.0, 127.4, 133.5, 136.0, 141.6, 148.8 (SiCH=CH), 148.9 and 149.2; δ_{Si}(79.5 MHz; $CDCl_3$; Me_4Si) −78.3 (O_3Si); *m/z* (MALDI) 2330.30 (M. $C_{128}H_{120}Si_8O_{28}$ requires 2329.92).

(**H2**) (271 mg, 63% based on unreacted **M2**); *m/z* (CI) 453.2064 (M+1. $C_{30}O_4H_{29}$ requires 453.2066).

Dimethyl 4′-vinylbiphenyl-3,5-dicarboxylate (M3)

A mixture of dimethyl 5-iodobenzene-1,3-dicarboxylate[38] (755 mg, 2.36 mmol), 4-styrene boronic acid (436 mg, 2.95 mmol), $[Pd(PPh_3)_4]$ (82 mg, 0.071 mmol), K_2CO_3 (2M, 4.2 mL, 8.40 mmol) and THF (70 mL) was heated at 75 °C for 48 hours. After cooling to room temperature, CH_2Cl_2 (50 mL) and water (20 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$. The residue was loaded onto a silica gel column and eluted with CH_2Cl_2 to afford **M3** as a white powder (531 mg, 76%) (Found: C, 73.0; H, 4.6. $C_{18}H_{16}O_4$ requires C, 73.0, H 5.4%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 3.99 (6 H,s, OCOCH3), 5.33 (1 H, d, $^3J_{HH}$ 11.1, CH_2=CH), 5.83 (1 H, d, $^3J_{HH}$ 17.8, CH_2=CH), 6.78 (1 H, dd, $^3J_{HH}$ 11.1, $^3J_{HH}$ 17.8, CH_2=CH), 7.53 (2 H, d, $^3J_{HH}$ 8.3), 7.65 (2 H, d, $^3J_{HH}$ 8.3), 8.48 (2 H, d, $^4J_{HH}$ 1.6) and 8.65 (1 H, t, $^4J_{HH}$ 1.6); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 52.6 (OCOCH3), 114.8 (CH_2=CH), 127.0, 127.5, 129.5, 131.3, 132.3, 136.3, 138.0, 138.4, 141.7 and 166.2 (OCOCH3); *m/z* (CI) 297.1129 (M+1. $C_{18}H_{17}O_4$ requires 297.1127).

1,3,5,7,9,11,13,15-Octakis[2-{4 Dimethyl 4′-vinyl biphenyl-3,5-dicarboxylate}ethenyl]pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (S3)

An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under nitrogen with octavinylsilsesquioxane[37] (20 mg, 0.032 mmol) and dimethyl 4′-vinylbiphenyl-3,5-dicarboxylate **M3** (164 mg, 0.55 mmol) in CH_2Cl_2 (10 mL). The solution of Grubbs′ catalyst (1 mg, 0.001 mmol) in CH_2Cl_2 (3 mL) was injected in the mixture heated at 55 °C to maintain a gentle reflux. The reaction was stopped and cooled down to room temperature after disappearance of the vinyl signals in the ^{1}H NMR spectrum (90 hours). The mixture was filtered, concentrated and then precipitated by adding the crude product in CH_2Cl_2 to a solution of ethyl acetate (120 mL) and petroleum ether (40–60) (500 mL). The residue was loaded onto a silica gel column and 3 bands were eluted with a gradient of CH_2Cl_2 and EtOAc (CH_2Cl_2 (**M3**)→ CH_2Cl_2/EtOAc (20/1) (**H3**)→ EtOAc (**S3**)) affording (**S3**) as a white powder (54 mg, 62%) (Found: C, 61.8; H, 3.6. $C_{120}H_{88}O_{44}Si_8$ requires C, 62.3; H 4.3%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 3.99 (48 H, s, OCOCH3), 6.47 (8 H, d, $^3J_{HH}$ = 19.2, SiCH=CH), 7.50 (8 H, d, $^3J_{HH}$ 19.2, SiCH=CH), 7.68 (32 H, m), 8.49 (16 H, d, $^4J_{HH}$ 1.6) and 8.66 (8 H, t, $^4J_{HH}$ 1.6); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 52.7 (OCOCH3), 118.3 (SiCH=CH), 127.1, 127.4, 127.9, 131.3, 131.5, 137.8, 138.5, 141.3, 147.8 (SiCH=CH) and 166.4 (OCOCH3); δ_{Si}(79.5 MHz; $CDCl_3$; Me_4Si) −78.5 (O_3Si); *m/z* (MALDI) 2802.41 (M+Na. $C_{120}H_{88}O_{44}Si_8Na$ requires 2801.08).

(**H3**) (72 mg, 64% based on unreacted **M3**); δ_H(400.13 MHz; $CDCl_3$; Me_4Si) 4.00 (12 H, s, OCOCH3), 7.24 (2 H, s, CH=CH), 7.67 (4 H, d, $^3J_{HH}$ 8.5), 7.71 (4 H, d, $^3J_{HH}$ 8.5), 8.50 (4 H, d, $^4J_{HH}$ 1.7), 8.50 (4 H, d, $^4J_{HH}$ 1.7), 8.67 (2 H, d, $^4J_{HH}$ 1.7); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 52.6 (OCOCH3), 127.3, 127.5, 128.6 (CH=CH), 129.4, 131.3, 132.0, 137.2, 138.2, 141.4, and 166.3 (OCOCH3); *m/z* (CI) 565.1864 (M+1. $C_{34}O_8H_{29}$ requires 565.1860).

Acknowledgements

The authors gratefully acknowledge the Scottish Higher Education Funding Council (SHEFC, P.A.) and the EC (IDECAT Network of Excellence Grant No NMP3-CT-2005–011730, N. R. V.) for financial support. P.A. would like to thank the Scottish University Physics Alliance (SUPA) for funding his Advanced Research Fellowship and both the School of Physics and Astronomy at St Andrews and Prof. I.D.W. Samuel for their support.

References

1 F. Aulenta, W. Hayes and S. Rannard, *Eur. Polym. J.*, 2003, **39**, 1741.
2 C. Valerio, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais and D. Astruc, *J. Am. Chem. Soc.*, 1997, **119**, 2588.
3 F. Zeng and S. C. Zimmerman, *Chem. Rev.*, 1997, **97**, 1681.
4 R. P. Brinas, T. Troxler, R. M. Hochstrasser and S. A. Vinogradov, *J. Am. Chem. Soc.*, 2005, **127**, 11851.
5 J. Leclaire, R. Dagiral, S. Fery-Forgues, Y. Coppel, B. Donnadieu, A.-M. Caminade and J.-P. Majoral, *J. Am. Chem. Soc.*, 2005, **127**, 15762.
6 A. M. Caminade, V. Maraval, R. Laurent and J. P. Majoral, *Curr. Org. Chem.*, 2002, **6**, 739.
7 L. J. Twyman, A. S. H. King and I. K. Martin, *Chem. Soc. Rev.*, 2002, **31**, 69.
8 D. Astruc, K. Heuze, S. Gatard, D. Mery, S. Nlate and L. Plault, *Adv. Synth. Catal.*, 2005, **347**, 329.
9 L. H. Gade, *Dendrimer Catalysis*, Springer GmbH edn., Berlin, Germany, 2006.
10 H. Kobayashi and M. W. Brechbiel, *Curr. Pharm. Biotechno.*, 2004, **5**, 539.
11 B. Felber and F. Diederich, *Helv. Chim. Acta*, 2005, **88**, 120.
12 P. L. Burn, S.-C. Lo and I. D. W. Samuel, *Adv. Mater.*, 2007, **19**, 1675.
13 F. C. D. Schryver, T. Vosch, M. Cotlet, M. v. d. Auweraer, K. Mullen and J. Hofkens, *Acc. Chem. Res.*, 2005, **38**, 514.
14 J. Dobler, M. Pritzsche and J. Sauer, *J. Am. Chem. Soc.*, 2005, **127**, 10861.
15 A. R. Bassindale, D. J. Parker, M. Pourny, P. G. Taylor, P. N. Horton and M. B. Hursthouse, *Organometallics*, 2004, **23**, 4400.
16 J. Choi, J. Harcup, A. F. Yee, Q. Zhu and R. M. Laine, *J. Am. Chem. Soc.*, 2001, **123**, 11420.
17 M. Y. Lo, C. Zhen, M. Lauters, G. E. Jabbour and A. Sellinger, *J. Am. Chem. Soc.*, 2007, **129**, 5808.
18 M. Y. Lo, K. Ueno, H. Tanabe and A. Sellinger, *Chem. Rec.*, 2006, **6**, 157.
19 S.-C. Lo and P. L. Burn, *Chem. Rev.*, 2007, **107**, 1097.
20 P. André, G. Cheng, A. Ruseckas, T. van Mourik, H. Früchtl, J. A. Crayston, R. E. Morris, D. Cole-Hamilton and I. D. W. Samuel, *J. Phys,. Chem. B*, 2008, Accepted.
21 V. Balzani, P. Ceroni, S. Gestermann, C. Kauffmann, M. Gorka and F. Vogtle, *Chem. Commun.*, 2000, 853.
22 F. J. Feher, D. Soulivong and A. G. Eklund, *Chem. Commun.*, 1998, 399.
23 F. J. Feher, R. Terroba and J. W. Ziller, *Chem. Commun.*, 1999, 2153.
24 E. Rikowski and H. C. Marsmann, *Polyhedron*, 1997, **16**, 3357.
25 F. J. Feher, D. Soulivong, A. G. Eklund and K. D. Wyndham, *Chem. Commun.*, 1997, 1185.
26 Y. Itami, B. Marciniec and M. Kubicki, *Chem. Eur. J.*, 2004, **10**, 1239.
27 J. D. Froehlich, R. Young, T. Nakamura, Y. Ohmori, S. Li and A. Mochizuki, *Chem. Mater.*, 2007, **19**, 4991.
28 K. Wada, N. Watanabe, K. Yamada, T. Kondo and T.-A. Mitsudo, *Chem. Commun.*, 2005, 95.
29 A. R. Bassindale, Z. Liu, I. A. MacKinnon, P. G. Taylor, Y. Yang, M. E. Light, P. N. Horton and M. B. Hursthouse, *J. Chem,. Soc., Dalton Trans.*, 2003, 2945.
30 G. Cheng, N. R. Vautravers and D. J. Cole-Hamilton, *Org. Biomol. Chem*, DOI: 10.1039/B812140K.
31 D. Satas, and A. A. Tracton, *Coatings technology handbook*, 2nd edn., Marcel Dekker, New York, 2001.
32 I. B. Berlman, *Handbook of fluorescence spectra of aromatic molecules*, 2d edn., Academic Press, New York, 1971.
33 J. McKiernan, J. C. Pouxviel, B. Dunn and J. I. Zink, *J. Phys. Chem.*, 1989, **93**, 2129.
34 M. von der Auweraer, M. van den Zegel, N. Boens, F. C. Deschryver and F. Willig, *J. Phys. Chem.*, 1986, **90**, 1169.
35 M. Pope, and C. E. Swenberg, *Electronic processes in organic crystals and polymers*, 2nd edn., Oxford University Press, New York, Oxford, 1999.
36 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991–1024.
37 M. Voronkov, T. N. Martynova, R. G. Mirskov and V. I. Bely, *J. Gen. Chem. USSR (Engl. Transl.)*, 1979, **49**, 1328.
38 M. Mazik and A. Konig, *J. Org. Chem.*, 2006, **71**, 7854.