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Oligo(fluorenyleneethynylenegermylene)s and their metallopolymers†

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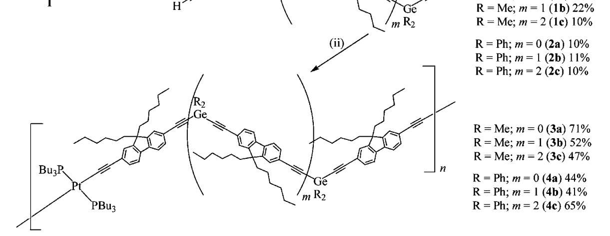
Oligo(fluorenyleneethynylenegermylene)s and their polyplatinynes are synthesized and photophysically characterized; inclusion of heavy germylene bridges greatly boosts the phosphorescence decay rate in metallopolymers.

The challenge of developing molecular systems composed of main group heteroatoms and acetylene units has had aesthetic appeal in recent years.[1] These acetylene-based scaffolds and their metal-capped congeners play a vital role in molecular optoelectronics.[2] While the study of oligo- and poly(aryleneethynylenesilylene)s represents an active research area,[3] little is understood on related systems with the heavier group 14 element germanium, and no oligo(aryleneethynylenegermylene)s of precise length and constitution have ever been described. We report here the unprecedented synthesis and photophysics of stable blue-emitting oligo(fluorenyleneethynylenegermylene)s (OFEG)s with alternating Ge and diethynylfluorene units. The first examples of Ge-bridged Pt(II) metallopolymers, derived from these oligomers, are also presented which display very fast phosphorescence decay rates. The triplet states in light-emitting diodes can be utilized in metal–organics through light-harvesting techniques.[4] To optimise this, work should focus on polymers with high energy triplets to avoid competition with nonradiative decay. Up till now, no reports on polymetallaynes with comparable radiative and nonradiative decay rate constants are known and it is highly desirable to achieve this goal for practical applications. The key feature of this study is the inclusion of a conjugation-interrupting sp^3-Ge linker that can limit the effective conjugation length (ECL) and trigger the triplet light emission by taking advantage of the heavy-atom effect of Ge atoms.

Lithiation of **I** by ^{n}BuLi in THF at -78 °C followed by germylation with R_2GeCl_2 ($R = Me, Ph$) gave a separable mixture of monodisperse OFEG **1a–c** and **2a–c** (Scheme 1). In both series, the yields of the dimers ($m = 1$) and trimers ($m = 2$) were increased at the expense of the monomers ($m = 0$) when more ^{n}BuLi was used. The merit of these short-chain oligomers over their polymeric counterparts lies in their precise molecular architectures, better solubility and their predetermined chemical composition.[5] These OFEGs are very organic-soluble and are fully characterized by NMR, IR and MS. The structures of **1a** and **2a** were confirmed by X-ray analyses (Fig. 1).[6] Stable polyplatinynes **3a–c** and **4a–c** were obtained by the dehydrohalogenative polymerization between *trans*-$[PtCl_2(PBu_3)_2]$ and the respective OFEG and their excellent film-forming properties and GPC data (Table 2) suggest a macromolecular nature for these materials. All the new compounds display excellent thermal stability in the TGA curves (Tables 1 and 2). The onset decomposition temperatures (T_{dec}) are almost invariant of the chain length and the R group. While *trans*-$[\text{-Pt(PBu}_3)_2\text{C}{\equiv}\text{C(9,9-dihexylfluorene-2,7-diyl)C}{\equiv}\text{C-}]_n$ **5** commences decomposition at 349 °C,[7] addition of a GeR_2 unit into the aryl-acetylene segment significantly increases the thermal stability of these Pt polyynes.



Scheme 1 *Reagents and conditions:* (i) ^{n}BuLi, -78 °C, R_2GeCl_2, THF; (ii) *trans*-$[PtCl_2(PBu_3)_2]$, CuI, NEt_3 CH_2Cl_2.

The absorption spectra of OFEG consist of organic $^1(\pi\pi^*)$ transitions in the near-UV region (Table 1), and a slight bathochromic shift in λ_{max} with increased extinction coefficients being observed for both series as m increases. But, the magnitude of red shifts rapidly decreases with increasing m value and there is no further significant shift in going from **2c** to the longer-chain polymer $[\text{-C}{\equiv}\text{C(9,9-dihexylfluorene-2,7-diyl)C}{\equiv}\text{CGePh}_2\text{-}]_n$ (λ_{max} = 346 nm). So, there would be little benefit for $m > 3$ in the control of spectral properties. The R groups on Ge exert minimal effect on the absorption energies. The transition energies of the Pt polymer are lowered relative to those of the OFEG, suggesting a well extended singlet excited state in the polymers. Examination of the absorption behavior of **1–4** in CH_2Cl_2 and in the solid state precludes any solid-state aggregates in thin films.

Our OFEGs are good light emitters and provide the best finite models for the Ge-containing poly(fluorenyleneethynylene)s. They emit remarkably strong purple-blue fluorescence at room temperature. The fluorescence quantum yields (Φ_F) of these oligomers are found to be chain length dependent and they increase down each series from **a** to **c** (*i.e.* $m = 2 > 1 > 0$). We also note that the Me compounds exhibit higher Φ_F than the Ph congeners and the emissions from **1b** and **1c** are highly efficient with Φ_F up to 0.92. These observations suggest that intrachain aggregation of luminophores may exist in these oligomers, and this interaction seemed to be more important as the chain length increases.[3a,8] While the presence of Ge can make the molecules more flexible, the opportunity for one chromophore unit to be located proximal to the other in space would increase with the molecular weight. The fluorescence radiative decay rate, $(k_r)_F$, is found to increase down each series or when passing from Ph to Me substituents. However, such fluorescence enhancement by increasing the m value tends to reach saturation up to $m = 3$ and Φ_F converges to a limiting value in their polymeric homologue ($n_{ECL} = 3$). For the Pt polymers,

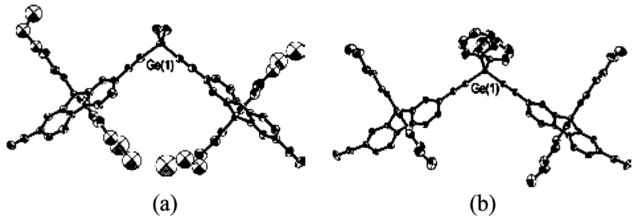


Fig. 1 ORTEP drawings of (a) **1a** and (b) **2a**.

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† Electronic supplementary information (ESI) available: experimental procedures and spectral data of all new compounds. See http://www.rsc.org/suppdata/cc/b4/b409580d/

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Table 1 Photophysical data (at 293 K) and thermal analyses of OFEG

OFEG	λ_{abs}/nm[a] (CH_2Cl_2)	λ_{abs}/nm (film)	E_{gap}/eV	λ_{em}/nm (CH_2Cl_2)	Φ_F[b]	τ_F/ns	$(k_r)_F/s^{-1}$	T_{dec}/°C
1a	337 (12.8)	339	3.57	362, 379	0.78	1.18	6.6×10^8	447
1b	343 (15.6)	343	3.51	368, 384	0.90	1.18	7.6×10^8	442
1c	344 (20.7)	345	3.49	369, 386	0.92	1.16	7.9×10^8	442
2a	339 (13.0)	341	3.54	364, 379	0.35	1.09	3.2×10^8	442
2b	345 (16.9)	347	3.49	371, 386	0.66	1.08	6.1×10^8	446
2c	346 (22.3)	348	3.47	371, 386	0.75	1.05	7.1×10^8	443

[a] ε (10^4 dm^3 mol^{-1} cm^{-1}) values are shown in parentheses. [b] Measured in CH_2Cl_2 relative to quinine sulfate in 0.1 N H_2SO_4 ($\Phi_F = 0.54$), $\lambda_{ex} = 313$ nm.

Table 2 Structural, thermal stability and emission data (at 20 K) of metallopolymers **3a–c** and **4a–c**

Polymer	M_w[a]	M_n[a]	T_{dec}/°C	λ_{em}/nm (film)	τ_P/μs	Φ_P	$(k_{nr})_P/s^{-1}$	$(k_r)_P/s^{-1}$
3a	42 970	13 580	410	412, 547	1.27	0.45	4.3×10^5	3.5×10^5
3b	22 950	11 150	414	411, 544	2.08	0.43	2.7×10^5	2.1×10^5
3c	22 790	16 150	407	410, 544	1.41	0.45	3.9×10^5	3.2×10^5
4a	23 970	10 400	404	414, 548	1.32	0.17	6.3×10^5	1.3×10^5
4b	28 350	12 830	407	411, 545	1.21	0.18	6.8×10^5	1.5×10^5
4c	22 600	17 550	418	411, 545	1.16	0.20	6.9×10^5	1.7×10^5

[a] Calibration against polystyrene standards.

both fluorescent and phosphorescent emissions arise from ligand-centred (ππ)* transitions. In dilute fluid solutions, we observe an intense ^{1}(ππ*) fluorescence peak near 400 nm for **3a–c** and **4a–c**, which do not display a large shift at high concentrations, excluding an excimer origin. At low temperatures, lower-lying spin-forbidden phosphorescence bands emerge at around 545 nm and the substantial Stokes shifts of these peaks from the dipole-allowed absorptions, plus the long emission lifetimes in the microsecond range are suggestive of their triplet parentage, and they are assigned to the ^{3}(ππ*) states of the organic chromophores. The triplet energy does not vary much with oligomer chain length, *i.e.* the lowest T_1 state is confined to a single repeat unit. Variation of the R group does not seem to alter this strong confinement. Insertion of a conjugation hindered GeR_2 group in **3** and **4** shifts the phosphorescence bands to the blue relative to **5**.[7] Values of $\Delta E(S_o–T_1)$ (energy gap between S_o and T_1) are found to be *ca.* 2.27–2.28 eV for both series. This corresponds to $S_1–S_0$ gaps of ~3.0 eV. The $\Delta E(S_1–T_1)$ values lie within the narrow range of 0.73–0.75 eV, in line with the $S_1–T_1$ energy gap of 0.7 ± 0.1 eV for metal polyynes of group 10–12 elements.[9]

The phosphorescence lifetimes (τ_P), quantum yields (Φ_P), and radiative ($(k_r)_P$) and nonradiative ($(k_{nr})_P$) decay rates at 20 K are listed in Table 2. Although the measured Φ_P values are relatively insensitive to the value of *m*, they are found to vary with the ER_2 group (E = Si, Ge). The $GeMe_2$ systems give more efficient phosphorescence than the $GePh_2$ congeners by over 2 times. But, replacement of $GePh_2$ by $SiPh_2$ reduces Φ_P by almost half ($\Phi_P \sim$ 10–13% for a $SiPh_2$ system) that can be correlated to the heavy-atom effect associated with the Ge atoms in the former case. The markedly different properties exhibited by these germylene polymers compared with their silylene analogues are mirrored by differences in other pairs of Ge and Si systems.[10] The $(k_r)_P$ values at 20 K are (2.1–3.5) × 10^5 s^{-1} for **3a–c** and (1.3–1.7) × 10^5 s^{-1} for **4a–c**. Relative to **5** ($(k_r)_P \sim 4.4 \times 10^4$ s^{-1}), insertion of the germylene component can increase $(k_r)_P$ by about 1 order of magnitude. Now, we are able to get comparable orders of magnitude for $(k_{nr})_P$ and $(k_r)_P$ which have never been observed in polymetallaynes reported so far. For phosphorescence in aromatic hydrocarbons, $(k_r)_P$ lies typically between 0.1 and 1 s^{-1}.[11] So, heavy-atom derivatization using Pt and Ge atoms together with conjugation interruption by the latter can greatly boost $(k_r)_P$ values by *ca.* 5 orders of magnitude. It is likely that the high energy benzene stretching modes of the Ph group is efficient at promoting $(k_{nr})_P$ for **4a–c**, making Φ_P and $(k_r)_P$ values smaller than those in **3a–c**.

In summary, we have developed a novel approach based on the heavy Ge conjugation-interrupter in metallopolymers that can limit ECL and result in much larger $(k_r)_P$ values. The present work has great potential to excel in optoelectronics that demand light energy harvesting from the T_1 state and one can take benefit from the large yield and radiative decay rate of triplet excitons.

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Notes and references

1 (*a*) P. Nguyen, P. Gómez-Elipe and I. Manners, *Chem. Rev.*, 1999, **99**, 1515; (*b*) C. D. Entwistle, A. S. Batsanov, J. A. K. Howard, M. A. Fox and T. B. Marder, *Chem. Commun.*, 2004, 702; (*c*) *Modern Acetylenic Chemistry*, ed. P. J. Stang and F. Diederich, Wiley-VCH, Weinheim, 1995.

2 (*a*) N. J. Long and C. K. Williams, *Angew. Chem., Int. Ed.*, 2003, **42**, 2586; (*b*) U. H. F. Bunz, *Chem. Rev.*, 2000, **100**, 1605; (*c*) I. Manners, *Synthetic Metal-Containing Polymers*, Wiley-VCH, Weinheim, 2004.

3 (*a*) R. J. P. Corriu, *Angew. Chem., Int. Ed.*, 2000, **39**, 1376; (*b*) W. E. Douglas, D. M. H. Guy, A. K. Kar and C. Wang, *Chem. Commun.*, 1998, 2125.

4 (*a*) X. Gong, M. R. Robinson, J. C. Ostrowski, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2002, **14**, 581; (*b*) M. A. Baldo, M. E. Thompson and S. R. Forrest, *Nature*, 2000, **403**, 750; (*c*) A. Köhler, J. S. Wilson and R. H. Friend, *Adv. Mater.*, 2002, **14**, 701.

5 (*a*) R. E. Martin and F. Diederich, *Angew. Chem., Int. Ed.*, 1999, **38**, 1350; (*b*) *Electronic Materials: The Oligomer Approach*, ed. K. Müllen and G. Wegner, Wiley-VCH, Weinheim, 1998.

6 Crystal data for **1a**: $C_{60}H_{72}Ge$, M_w = 865.82, monoclinic, space group *C2/c*, *a* = 33.747(2), *b* = 10.2041(5), *c* = 31.427(1) Å, β = 91.242(1)°, *V* = 10819.8(9) $Å^3$, *Z* = 8, μ(Mo–Kα) = 0.600 mm^{-1}. 65722 reflections measured, 26369 unique, *R*(int) = 0.106. Final *R* = 0.0860 and R_w = 0.1050 for 4866 observed reflections with $I > 1.5\sigma(I)$. For **2a**: $C_{70}H_{76}Ge$, M_w = 989.96, monoclinic, space group *P2/c*, *a* = 9.1566(7), *b* = 12.0396(9), *c* = 26.852(2) Å, β = 97.021(2)°, *V* = 2938.0(4) $Å^3$, *Z* = 2, μ(Mo–Kα) = 0.560 mm^{-1}.17699 reflections measured, 7122 unique, *R*(int) = 0.038. Final *R* = 0.0510 and R_w = 0.0530 for 4172 observed reflections with $I > 1.5\sigma(I)$. CCDC 237762–237763. See http://www.rsc.org/suppdata/cc/b4/b409580d/ for crystallographic data in .cif or other electronic format.

7 W.-Y. Wong, G.-L. Lu, K.-H. Choi and J.-X. Shi, *Macromolecules*, 2002, **35**, 3506.

8 Y.-J. Miao, W. G. Herkstroeter, B. J. Sun, A. G. Wong-Foy and G. C. Bazan, *J. Am. Chem. Soc.*, 1995, **117**, 11407.

9 (*a*) J. S. Wilson, N. Chawdhury, M. R. A. Al-Mandhary, M. Younus, M. S. Khan, P. R. Raithby, A. Köhler and R. H. Friend, *J. Am. Chem. Soc.*, 2001, **123**, 9412; (*b*) H.-Y. Chao, W. Lu, Y. Li, M. C. W. Chan, C.-M. Che, K.-K. Cheung and N. Zhu, *J. Am. Chem. Soc.*, 2002, **124**, 14696; (*c*) W.-Y. Wong, L. Liu and J.-X. Shi, *Angew. Chem., Int. Ed.*, 2003, **42**, 4064.

10 (*a*) A. C. Spivey, D. J. Turner and S. Yeates, *Org. Lett.*, 2002, **4**, 1899; (*b*) J. L. Bréfort, R. J. P. Corriu, Ph. Gerbler, C. Guérin, B. J. L. Henner, A. Jean, Th. Kuhlmann, F. Garnier and A. Yassar, *Organometallics*, 1992, **11**, 2500.

11 (*a*) N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, Mill Valley, CA, USA, 1991.