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Polyferrocenes: metallopolymers with tunable and high refractive indices†

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The refractive index, molar refraction and Abbé number of polyferrocene derivatives are reported and the values indicate that these materials are very promising for a range of photonics applications.

Progress in developing and fabricating new photonic devices depends on the availability of materials with appropriate optical properties. Polymers offer ease of functionalization and low processing cost. Additionally, due to their inherent flexibility, polymers can be used in devices with a complicated design. Unfortunately, in contrast to traditionally used inorganic glasses, organic polymers possess a narrow range of refractive indices.[1] Since many present and proposed photonic devices are based on microcomponents with a high refractive index contrast, the applicability of polymers in such devices is limited.[2–4]

In response to this shortcoming, molecular tailoring of macromolecules with functional groups varying in electronic polarization is used to expand the refractive index (RI) range of polymers.[5] For instance, highly polarizable π-conjugated functionalities incorporated into organic polymers increase their RI. Unfortunately, π-conjugation brings drawbacks such as high optical dispersion, light absorption, and birefringence.[5] Furthermore, as a general approach, molecular tailoring is constrained by the availability of functional groups, maintaining the upper limit of the refractive index of organic polymers near 1.6.[1] Alternatively, the incorporation of inorganic clusters into a polymer matrix can be used as a means of increasing the refractive index of polymers; however the weaknesses of heterogeneous structures include higher optical loss and poor processability. A more promising strategy involves the incorporation of high molar refraction elements such as S, P, and Pb, into macromolecules which increases the RI without significantly increasing the optical dispersion of the material.[6–8]

Previous studies on polyferrocenylsilanes[9] demonstrated their potential as materials for optical-fiber sensing and tunable photonic devices.[10,11] To date, however, the optical properties of these and other polyferrocenes remain virtually unexplored. In this communication, we demonstrate that the class of polyferrocene polymers possesses unusually high RI values which can be further increased by tailoring the backbone with high molar refraction substituent groups.‡

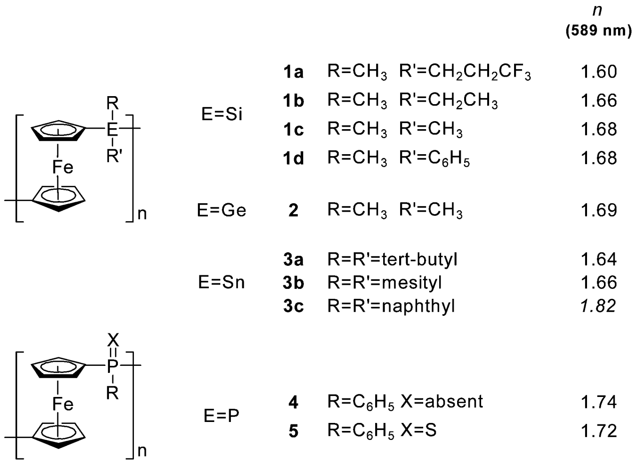
The structures of polyferrocene derivatives synthesized by ring-opening methodologies,[12–16] are given in Fig. 1, along with the corresponding RI values measured at λ = 589 nm (Sopra GES-5 ellipsometer). For polyferrocenylsilanes (series **1**), we show the possibility of tuning the refractive index by varying the substituent groups: from lower values *via* fluorination (n = 1.60 for **1a**) to higher values *via* arylation (n = 1.68 for **1d**). Additional tuning of the refractive index was accomplished by changing the spacer element (E), as exemplified with **1c** and **2** for the same substituent groups, and for **3–5** for different substituent groups. Polyferrocenylphosphines and polyferrocenylphosphine sulfides (**4** and **5**) showed unusually high RI values (n = 1.74 and n = 1.72, respectively).

Further characterization of the optical properties of polyferrocenes was performed by extracting their molar refraction. We used the Lorentz and Lorenz equation [eqn. (1)][17] which expresses the molar refraction (R_M) of the repeating unit in terms of n and the molar volume (V_M) of a polymer repeating unit. Since the molar refraction is an additive term (ΣR_i), where R_i is the molar refraction of the functional group, for each repeating unit we subtracted from R_M the molar refraction of the substituent groups.[17] In this fashion, we obtained the molar refraction of the backbone unit, R_{fcE}, where fc is the ferrocene unit and E is the spacer element. We found R_{fcE} to be 57.2, 58.9, 63.2, and 62.5 cm^3 mol^{-1} for fcSi, fcGe, fcSn and fcP, respectively. We note that these values are significantly higher than those of other inorganic polymers. For instance, the molar refraction of the [N=P] repeating unit of polyphosphazenes is 14.36 cm^3 mol^{-1}. [8]

$$\frac{n^2-1}{n^2+2}V_M = R_M = \sum_i R_i \tag{1}$$

The values of R_{fcE} allowed us to predict refractive indices for polyferrocenes with different substituent groups (for which the values of R_i are known).[17] For instance, the large R_M value of 63.2 cm^3 mol^{-1} for the fcSn repeating unit showed the potential of further increasing the RI to 1.82 for a hypothetical polyferrocenylstannane **3c** tailored with naphthyl substituent groups.

Since at optical frequencies the extent of light-induced polarization of electrons from their equilibrium position relative to the nuclei is directly related to the molar refraction of a medium [eqn. (2)],[17] we plotted R_{fcE} *vs.* the atomic polarizability of the spacer element (α_E). In Fig. 2 the slope of 2.72 × 10^{24} mol^{-1} obtained from the regression for group 14 elements is comparable to the slope of 2.52 × 10^{24} mol^{-1} expected from eqn. (2). A small discrepancy between the experimental and theoretical values resulted from the assumption that the spacer elements are in an unbound state.[18] This discrepancy was more significant for the molar refraction of the fcP group which did not follow the trend of



E				n (589 nm)
E=Si	**1a**	R=CH$_3$	R'=CH$_2$CH$_2$CF$_3$	1.60
	1b	R=CH$_3$	R'=CH$_2$CH$_3$	1.66
	1c	R=CH$_3$	R'=CH$_3$	1.68
	1d	R=CH$_3$	R'=C$_6$H$_5$	1.68
E=Ge	**2**	R=CH$_3$	R'=CH$_3$	1.69
E=Sn	**3a**	R=R'=tert-butyl		1.64
	3b	R=R'=mesityl		1.66
	3c	R=R'=naphthyl		*1.82*
E=P	**4**	R=C$_6$H$_5$	X=absent	1.74
	5	R=C$_6$H$_5$	X=S	1.72

Fig. 1 Refractive index determined at λ = 589 nm for polyferrocenes. The refractive index value of the hypothetical compound **3c** was predicted using eqn. (1).

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† Electronic supplementary information (ESI) available: synthesis of polyferrocenes, film preparation and ellipsometric characterization. See http://www.rsc.org/suppdata/cc/b3/b311934c/

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fcE for group 14 elements (Fig. 2). In contrast with group 14 elements, the P-center in polyferrocene **4** is trivalent with a nonbonding pair of electrons. Therefore, for P a higher molar value of refraction per polarizability presumably expressed the stronger propensity of nonbonding electrons to be polarized by an applied electric field. Previous studies of phosphorus compounds showed that their molar refractivity strongly depends on P valency.[19,20]

$$R_{\mathrm{fcE}} = \left(\frac{4\pi N_{\mathrm{A}}}{3}\right)\alpha_{\mathrm{E}} + \left(\frac{4\pi N_{\mathrm{A}}}{3}\right)\alpha_{\mathrm{fc}} \tag{2}$$

We also used the y-intercept of the group 14 regression to calculate the molar refraction of ferrocene in polyferrocenes. We found an extrapolated R_{fc} of 43.6 $\mathrm{cm^3\ mol^{-1}}$. This value is comparable to a previous value of 50.4 $\mathrm{cm^3\ mol^{-1}}$ found for molecular ferrocene by Aroney *et al.*[21]

Optical dispersion of polyferrocenes **1–5** (Fig. 1) was expressed as the Abbé number, ν_{D}:[1]

$$\nu_{\mathrm{D}} = \frac{n_{\mathrm{D}} - 1}{n_{\mathrm{F}} - n_{\mathrm{C}}} \tag{3}$$

where n_{D}, n_{F}, and n_{C} are the refractive indices at 589, 486 and 656 nm, respectively. To demonstrate the optical merits of polyferrocenes, we adapted the data of Dislich[1] showing the relationship between the Abbé number (optical dispersion) and the refractive indices for inorganic glasses and organic polymers. In Fig. 3, the dotted and the hatched areas show the range of Abbé numbers and the associated refractive indices for purely organic polymers and for inorganic glasses, respectively. Polyferrocenes have a substantially higher Abbé number (lower dispersion) than organic polymers with the same refractive indices. Fig. 3 also shows that for the same dispersion polyferrocenes possess significantly higher values of RI than organic polymers (*e.g.* see dotted line for $\nu = 23$). Thus the main group spacer elements prove to be efficient in increasing the refractive index of a polymer without increasing its optical dispersion. Overall, polyferrocenes have an intermediate position between organic polymers and inorganic glasses.

In summary, we showed that polyferrocenes have exceptionally high refractive indices at relatively low optical dispersion. We also found that polyferrocenes have inherently high molar refraction, in comparison with other inorganic polymers. This feature provides great promise for achieving higher values of refractive index by attaching deliberately chosen side groups with high molar refraction.

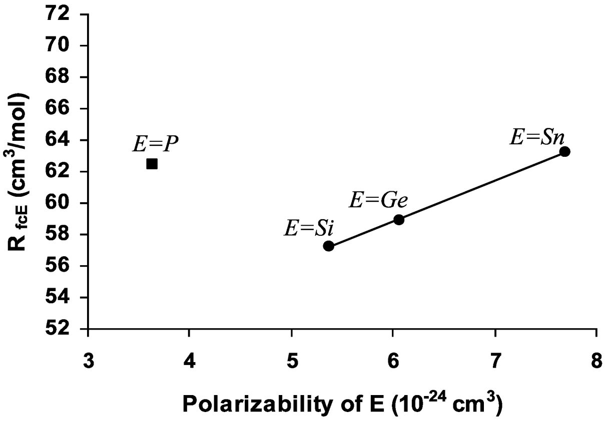

Fig. 2 Relationship between molar refraction of the fcE unit of polyferrocenes and atomic polarizability of E. The circles correspond to group 14 elements and the square represents a group 15 element (E = P)

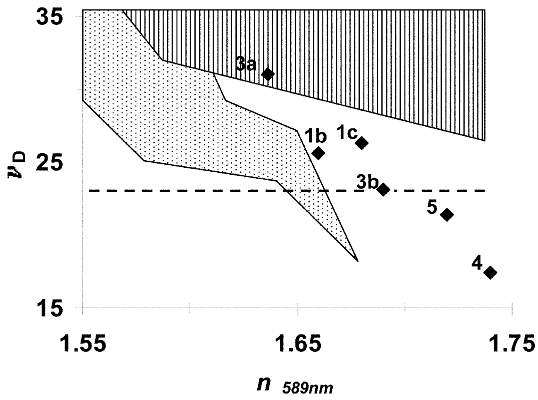

Fig. 3 Relationship between Abbé number and refractive index for organic polymers (dotted area), for the inorganic glasses (hatched area) and for various polyferrocenes.[1] The experimental points correspond to polymers whose structures are shown in Fig. 1.

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Notes and references

‡ Polyferrocenes exhibit Laporte forbidden d–d transition near $\lambda = 440$ nm. This transition is very weak and it does not significantly change the polymer refractive index.

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