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Gas Response Behaviour and Photochemistry of Borondiketonate in Acrylic Polymer Matrices for Sensing Applications

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Abstract The fluorescent spectra in combination with gas response behavior of acrylic polymers doped with dibenzoyl(methanato)boron difluoride ($DBMBF_2$) were studied by fluorescence spectroscopy and time-resolved fluorescence lifetime. The role of acrylic matrix polarity upon the fluorescence spectra and fluorescence lifetime was analyzed. Changes in emission of the dye doped polymers under exposure to toluene, n-hexane and ethanol were monitored. The fluorescence lifetimes were measured for the singlet excited state as well as the exciplex formed between $DBMBF_2$ and toluene. A reduction of the transition energy to the first singlet-excited state in the four polymers was observed, compared to solution. Reversible exciplex formation, viz. a red shifted fluorescence emission was perceived when exposing the polymers to toluene, while for hexane and ethanol only reversible reduction of the fluorescence occurred. Longer singlet and shorter exciplex lifetimes were observed for non-polar matrixes. The latter mechanism is explained in function of the lower charge transfer character of the exciplex in non-polar matrixes. Additionally, the quantum yield of the dye in the polymer matrix increased almost seventh-fold compared to values for solution.

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Introduction

The family of beta-diketone-boron difluoride complexes are known in literature for over 75 years. Their properties and behavior have been extensively studied, due to their attractive features including high fluorescent quantum yields and molar absorption coefficients [1, 2], two photon absorption [3], strong dependence of emission upon chemical environment [3–5] and their multiple photoreactions with unsaturated hydrocarbons [6, 7]. One of the compounds of this family, dibenzoyl(methanato)boron difluoride ($DBMBF_2$) has shown potential as a fluorescent probe for gas sensing applications. The photoluminescence of $DBMBF_2$ and some of its derivatives show changes upon exposure to oxygen [8], humidity and aromatic compounds. Recently, Fraser et al. demonstrated materials based on beta-diketone-boron difluoride complexes showing responsive behavior to temperature and mechanical force [9–11].

The appearance of a new fluorescent band of $DBMBF_2$ in solution after the addition of substituted monocyclic aromatic hydrocarbons (MAH) such as benzene, toluene and xylene, together with the quenching of the original fluorescence was first observed by Chow et al. [6, 7]. This new fluorescent band in the form of a red-shifted, structureless emission was assigned to the radiative relaxation of an excited complex viz. exciplex between $DBMBF_2$ and the aromatic compound. The exciplex, a non-covalent aromatic interaction between the $DBMBF_2$ and the aromatic compound provides a fully reversible complex. The emission maximum was shown to shift to longer wavelengths with decreasing ionization potential of the substituted aromatic and the emission intensity to be

dependent on the concentration [12, 13]. This new emissive species has been associated to a 1:1 reversible exciplex between DBMBF$_2$ and the substituted benzene, though higher stoichiometry complexes have been observed at high donor concentration [14]. The transition from the ground state to the excited state was found to be accompanied by a small dipole change of ~1.5D from a highly polar ground state (6.7D) [15]. The emission spectra, quantum yields and fluorescent lifetimes of the fluorophore were shown to be sensitive to the solvent environment of the fluorophore, including to properties such as polarity [3], viscosity [16], and temperature [1, 4, 15]. This exciplex formation upon exposure to MAH was recently reported for DBMBF$_2$ absorbed over solid inorganic supports, such as silica plates [17], and covalently linked to silica nanoparticles [18].

Widespread exposure of humans to MAH and in particular benzene and toluene at concentrations of part per million poses major health hazards. A major issues is however the lack of sensors principles capable of selectively and reversibly detecting these gases. The unique optical characteristics (*viz.* exciplex) of the DBMBF$_2$ dye provides such properties making it a promising candidate for the development of a selective and reversible solid state optical probes for the detection of such aromatic compounds.

Whereas inorganic supports have been used, polymer matrices have clear benefits. Polymers have the advantage of tunability in terms of chemical and physical properties by careful selection of their composition. Regarding processing, the material can easily be made into thin films, nano and micro particles or other morphologies that can be integrated into various optical sensors, such as waveguides, optical fibers and membranes [19, 20]. By chemical modification, the dye can be grafted onto the backbone of the polymer chain, which improves dye stability and material homogeneity, by reducing aggregation or precipitation at high dye concentrations and by protecting from chemical degradation [21]. Whereas the dispersion of the DBMBF$_2$ dye in polymeric matrices, such as polymethylmethacrylate [22] or polylactic acid has been reported, analysis of the exciplex formation within such matrices is lacking [23]. The limited understanding of the exciplex formation in polymers matrices hampers further sensor development for MAH based on this class of materials.

It is imperative to understand fluorophore-polymer interaction in combination with the polymer host properties such as porosity, polarity, or permeability, critical for developing dye-doped polymers for gas sensing applications. In this study, we investigated the fluorescent properties and gas response of DBMBF$_2$ immobilized in acrylic based polymers. The selection of acrylic monomers as a base material owes to the extensive library of chemical functionalities commercially available, allowing preparation of polymers with tuned physicochemical properties. To understand the influence of polarity and crystallinity upon the absorption, emission, fluorescent

lifetimes of the DBMBF$_2$ fluorophore, the acrylic based polymers were tailored with varying polarities and the glass transition temperatures. The influence of these parameters on the fluorescence under exposure to toluene, n-hexane and ethanol gases was studied. The formation and emission of the exciplex between DBMBF$_2$ and toluene as a function of matrices is discussed.

Experimental Section

Materials

Lauryl acrylate (90 %), isodecyl acrylate, di(ethylene glycol) ethyl ether acrylate (>90 %), tetrahydrofurfuryl acrylate and 1,1′-azobis(cyclohexanecarbonitrile) were purchased from Sigma-Aldrich and used without further purification.

Dibenzoyl(Methanato)Boron Difluoride (DBMBF$_2$) Synthesis Procedure

Dibenzoyl(methanato)boron difluoride (DBMBF$_2$) was obtained by the reaction of the dibenzoylmethane with boron trifluoride diethyl etherate in dichloromethane. The product was purified by recrystallization from toluene. Subsequently borontrifluoride diethyl etherate (0.012 mol) was added to a solution of dibenzoylmethane (0.01 mol) in dry dichloromethane (30 mL). The reaction mixture was stirred for 1 h at room temperature. After removing the solvent by evaporation in vacuo, the residue was purified by recrystallization from toluene. Yield: 74 %, mp 193–195 °C. 1H NMR (300 MHz, CDCl3): δ 7.20 (s, 1H, CO-CH-CO), 7.56 (t, 4H, J=7.6 Hz, Ph), 7.70 (t, 2H, J=7.3 Hz, Ph), 8.15 (d, 4H, J=7.3 Hz, Ph).

Fabrication of DBMBF$_2$ Fluorophore Doped Polymers

DBMBF$_2$ doped polymers were fabricated from acrylic monomers. In this study, two non-polar monomers isodecylacrylate (mC10a) and dodecylacrylate (mC12a) and two polar, non-protic monomers tetrahydrofurfuryl acrylate (mTHFa) and diethyleneglycol ethyl ether acrylate (mDEGa), were used. The homopolymers derived from these monomers are referred to as pC10a, pC12a, pTHFa and pDEGa respectively (chemical structures are given in Fig. 1). Due to the absence of information of the dielectric constant of the homopolymers obtained from these monomers, solubility parameters were used in order to obtain an approximation of the polarity and solvent properties of the polymers. For that purpose, the Hansen Solubility Parameters [24, 25] of four compounds structurally related to the precursor monomers were taken (see Table 1). The parameters represent the energy from dipolar (δ_P), dispersive (δ_D), and hydrogen bonding (δ_H) forces between molecules in solution. These parameters were
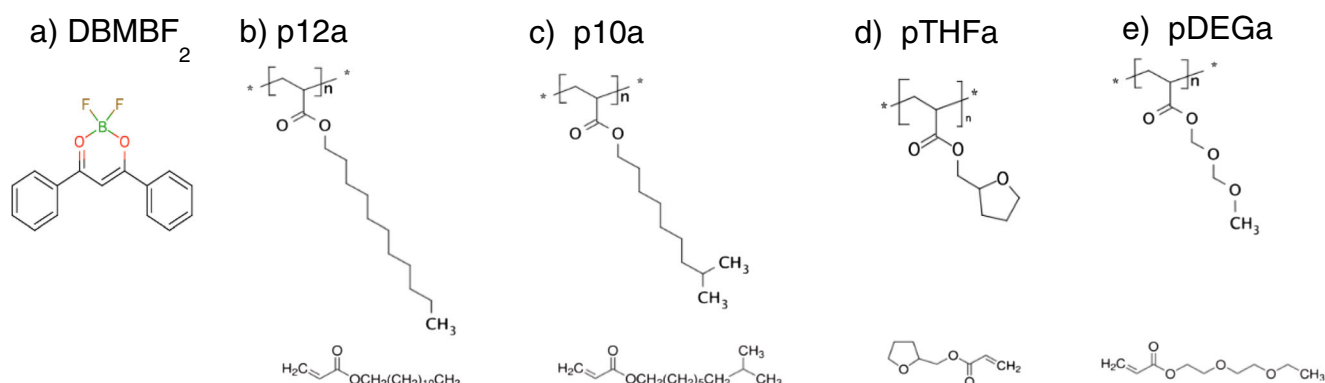
Fig. 1 a chemical structure of dibenzoyl(methanato)boron difluoride (DBMBF2) dye. b. p12a polymer structures and corresponding dodecyl acrylate monomer structure c p10a polymer structures and corresponding isodecyl acrylate monomer structure d pTHFa polymer structures and corresponding tetrahydrofurfuryl acrylate monomer structure e pDEGa polymer structures and corresponding dietheylglycol acrylate monomer structure

used to compare the influence of the polymer on the fluorescent properties of DBMBF$_2$. The four structurally related reference compounds were decane(C10), dodecane (C12) 2-methyl tetrahydrofuran (2-MeTHF) and diethylene glycol diethyl ether (DEG).

The monomers were selected such that the homopolymers obtained showed significant differences in the glass transition temperatures (T$_g$) between each polar and non-polar polymer(see Table 1) while all T$_g$'s remained well below room temperature ensuring a rubbery state of the matrices. A rubbery and amorphous polymer favors an even distribution of the dye throughout the matrix [26]. The thermal initiator used for the polymerization was 1,1′-azobis(cyclohexanecarbonitrile). It does not produce oxygenated residues [27], does not cause oxidative degradation of pigments or dyes and is highly soluble in nonpolar monomers. The initiator was added in a concentration of 0.5 % mass/mass to the monomers, and the solutions were ultrasonicated for 10 min and then mixed over a stirrer for additional 30 min to ensure complete mixing of the initiator.

The solubility of the dye in the different monomers was estimated using the software HSPiP [28]. For the calculations, a molecular volume of 41.8 Å^3 was used, obtained by the QSAR method [29].

A solution of DBMBF$_2$ (6.2 mM in n-propyl acetate) was added to the monomers in a proportion of 100 μL/500 mg of monomer and then mixed, to give solutions with an approximate concentration of 2.2 mmolal (relative to the mass of the monomer). N-propyl acetate was selected as solvent for its compatibility with acrylate monomers and polymers. This ensures no solid/liquid separation during polymerization. The formulations were used to prepare layers and monoliths of the polymerized monomers. Thin layers were prepared by drop casting the mixtures over quartz slides (1×1cm) cleaned in an UV/O$_3$ reactor. To polymerize the mixtures, the glass slides were placed overnight over a hot plate at 80 °C, under a nitrogen flow. Polymerization was done in a dark environment to prevent any photoreactions between the dye and the monomers, as it has been reported previously [30]. For the production of the thick monoliths, 0.5 mL glass vials were filled with 0.25 mL of the mixtures and sealed with a septum. The vials were placed over a hot plate at 90 °C, and flushed continuously with N$_2$. The polymerization was carried out overnight.

Fluorescent Measurements

A fluorescence spectrophotometer (Edinburgh FLSP920) was used to measure excitation, and fluorescence spectra, together with the fluorescence lifetimes. For the excitation spectra, the emission was monitored at 420 nm using a Xenon arc lamp as the source of excitation. For the measurement of the fluorescence emission and lifetimes, a LED laser (Edinburgh EPL 375) at 375 nm was used as excitation source. Excitation and emission spectra were recorded from all the fluorophore containing polymer layers.

Table 1 Hansen solubility parameters (δD, δP, δH), dielectric constant for reference solvents (ε), glass transition temperature (T$_g$) of homopolymers and solubility estimate of DBMBF$_2$ in monomers

Polymer	Monomer	Solvent	δ$_D$	δ$_P$	δ$_H$	ε	T$_g$	%m/m
pC12a	Dodecylacrylate	Dodecane	16	0	0	2	−30	1.88
pC10a	Isodecyl acrylate	Decane	16	0	0	2	−60	1.59
pTHFa	Tetrahydrofurfurylacrylate	2-methyltetrahydrofuran	16.9	5	4.3	6.9	−28	6.2
pDEGa	Diethylene glycol ethyl ether acrylate	Diethylene glycol diethyl ether	15.8	5.9	5.6	5.7	−54	2.64

Lifetimes were collected using the Time Correlated Single Photon Counting mode from the spectrophotometer. The same LED laser was used for excitation, with a pulse interval of 100 ns. Singlet lifetimes were collected from the doped polymer films deposited onto quartz slides. The emission was monitored at 400 nm. The decay curves were fitted with a monoexponential decay function (residuals of fitting available in *Supp. Info.* Fig. S2), as the singlet is the only specie expected to fluoresce at that wavelength (see Fig. 5). The fitting was performed between the maximum count number to $1/e$ of its value, to limit the contribution of the lifetime of additional excited species (i.e. excimers) and measuring artifacts on the value obtained for the singlet lifetime. Biexponential fitting of the decay curves was also applied, resulting in similar lifetimes as reported in Fig. 3, however with higher values for χ^2.

Exciplex lifetime spectra and lifetimes were obtained by exposing the polymer monoliths to saturated toluene vapors. The procedure consisted of loading the quartz slide with the doped polymer into a closed quartz cuvette containing a small volume of toluene. The sample was left to saturate with the toluene vapors for 10 min prior to measurements. The lifetimes of the exciplex decay were measured at 500 nm and fitted using a biexponential decay function. The longer component was assigned as the exciplex lifetime.

Gas Response Measurements

Changes in the fluorescent emission towards the exposure to toluene, hexane and ethanol were performed on monolith samples placed on quartz slides and introduced into a closed quartz cuvette with a small volume of the solvents. The fluorescent spectra were measured at 2, 4, 6, 8 and 10 min after introduction of the sample into the cuvette.

Results and Discussion

Dibenzoyl(methanato)boron difluoride (DBMBF$_2$) is a well-known compound with intense emission and quantum yields between 0.08 and 0.20 in solution and solid state [4, 12, 15]. The compound is characterized by a strong absorption in solution (33,000–46,000 μM^{-1} cm^{-1}) [3] in the near UV (350–390 nm) and an emission band between 390 and 550 nm. In comparison with its β-diketonate parent compound, DBMBF$_2$ has a more rigid molecular structure, which is reflected in its structured excitation and emission spectra and small Stokes loss (<1,000 cm^{-1}) [1].

Singlet Fluorescent Behavior

The excitation and emission spectra of DBMBF$_2$ in four different acrylate polymers is given in Fig. 2. As the emission
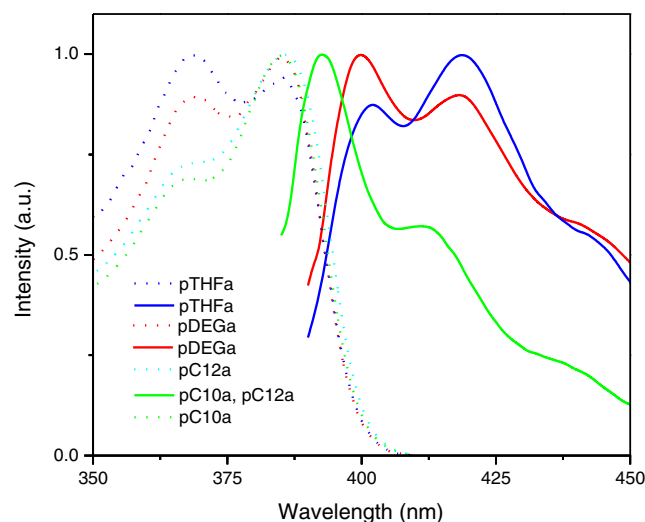
Fig. 2 Excitation (*dotted line*) and fluorescence (*solid line*) spectra of DBMBF$_2$ in p10a (*green*) and p12a (*cyan: excitation and green: fluorescence*) pTHFa (*blue*), pDEGa (*red*)

for DBMBF$_2$ originates from the lowest lying excited state, the absorption and excitation spectra coincide [1]. By measuring the excitation spectra instead of the absorption spectra, interference in the spectra originating from absorption of residual polymerization initiator can be circumvented. The non-conjugated character of the matrices ensures transparency at the scanning wavelengths. Two excitation maxima were found at 368 and 385 nm for all matrices, viz. pC10a, pC12a, pTHFa and pDEGa (see Fig. 2, dotted lines) albeit with different intensities. Though the polarities of pC10a and pC12a are very different from the polarities of pTHFa and pDEGa, the positions of the maxima are identical.

It is well known that the different solvation of the excited and ground state by the solvent lead to changes on the excitation and absorption wavelengths, through the phenomena known as solvatochromism. As for the case of DBMBF$_2$, the dipole of fluorophore increases during the transition, which should lead to a higher stabilization of the excited state compared to the ground state in polar media. This solvatochromic behavior was reported previously for solution of the dye [1, 15], but as mentioned above, no difference is observed in the excitation maxima for the doped polymers. This indicates that regardless the difference of polarity of the polymers, the solvation of the dye (in ground and excited states) is very similar within the matrices during the absorption/excitation process.

Nevertheless, the excitation maxima in the polymers differ from the values reported from solution. Johanson et al. [1] reported absorption maxima at 359, 363, and 364 nm for DBMBF$_2$ in hexane, dichloromethane and acetonitrile, respectively, 5–9 nm shorter than the values measured in the acrylic polymers. The longer excitation wavelengths of the doped polymers compared to the solutions can be understood by taking into account the higher viscosity of the polymers.

The increased viscosity of the environment for the polymer leads to a shift of the excitation wavelength towards the red-edge of the absorption band. This phenomena is sometimes referred as red edge excitation shift (REES) [31]. We also observed that the intensity of the peak at 385 nm was stronger than the peak at 368 nm for the less polar matrixes. Zhang reported similar excitations spectra where the longer wavelength shoulder prevails. The difference of the spectra in the more polar matrixes, in particular pTHFa, is not clearly understood. The changes of aggregation or solubility have been suggested previously to explain spectral changes of fluorescent dyes [21]. At the concentration used in the preparation of the dye/monomer solution (~2.2 mmolal) no observation of aggregation has been reported [32]. Though aggregation of the dye after polymerization could lead to ground state interactions that have been suspected of changes in the excitation spectra [23]. The solubility of the dye was lower in the less polar matrixes (see Table 1), which could justify a stronger aggregation on the later compared to the more polar pTHFa and pDEGa.

The fluorescence spectra exhibit large wavelength shifts in emission between the different polymers, as seen in Table 2. For thin polymer films presented in Fig. 2, longer emission wavelengths are observed in the order pC10a, pC12a < pDEGa < pTHFa, with a difference of 7–8 nm between the non-polar matrixes (pC10a, pC12a) and the polar (pDEGa, pTHFa). Fluorescence spectra of thicker monolith films are presented in Fig. 4. Whereas the emission spectra for polar films (pDEGa, pTHFa) remained identical for layers and monoliths, the nonpolar monolith films (pC10a, pC12a) showed a significant red shift of the first emission peak presumably due to self-absorption resulting from the small Stokes shift of the dye and aggregation of the dye in the polymer [21]. The red-shift in emission for the polar matrixes, can be mainly explained due to solvatochromism [21, 33], as aggregation is unlikely for these matrixes as observed from the unaltered excitation spectra (Fig. 2) and higher dye solubility. In comparison to the excitation process, prior to the fluorescent emission, a reorganization of the polymer molecules around the fluorophore occurs. For polar matrixes, this process reduces the energy of the excited state resulting in a red-shifted emission. The observed solvatochromic effect should

reflect the polarity of the different polymer matrices. The Hansen Solubility Parameters (HSP) were used to predict the shifts of the emission maxima. For pTHFa and pDEGa, the HSP of 4-MeTHF and DEG were used to compare relative polarities between polymers. Nevertheless, it should be recognized that the assumptions are based only on structural similarities of the compounds and ignore the reduced mobility of the substructure units in the polymer chains. Table 1 shows that both 4-MeTHF and DEG present similar values for their polar (δ_p) and dispersive component (δ_d). Hence the similar solvatochromic shifts of the excited DBMBF$_2$ in pDEGa and pTHFa is in line with their expected solvation parameters. The same analysis holds for pC10a and pC12a, using as reference compound dodecane and decane. From the crossover of the excitation and emission spectra, the energy of the first singlet excited state was calculated for the thin films as well as thick layers (Table 2). For thin polymer films the energy decreases with the polymer polarity from 3.16 eV (pC10a, pC12a) to 3.11 eV (pTHFa) and 3.09 eV (pDEGa). The values are however lower than those obtained from the crossover of the excitation and emission spectra reported in solution [13].

The radiative decay of the DBMBF$_2$ fluorophore in the four polymer matrices is given in Fig. 3. The fluorescence lifetimes (τ_s) of the dye were found to be 1.03 ns (pC10a), 1.01 ns (pC12a), 0.99 ns (pDEGa) and 0.93 ns (pTHFa) for the different matrices. The single exponential fitting of the decay curves indicates the existence of only one emitting specie, discarding the presence of excimers.

Several values have been reported for the lifetimes of DBMBF2 in solution, ranging from 140 ps (cyclohexane) up to 370 ps (acetonitrile) [14, 15], about ten times shorter than the values obtained from the polymer films. Using the well-known expression, $\tau=(k_{NR}+k_R)^{-1}$, the longer lifetimes in the polymers should indicate a decrease of either the radiative rate (k_R), the non-radiative decay rate (k_{NR}) or from both. The
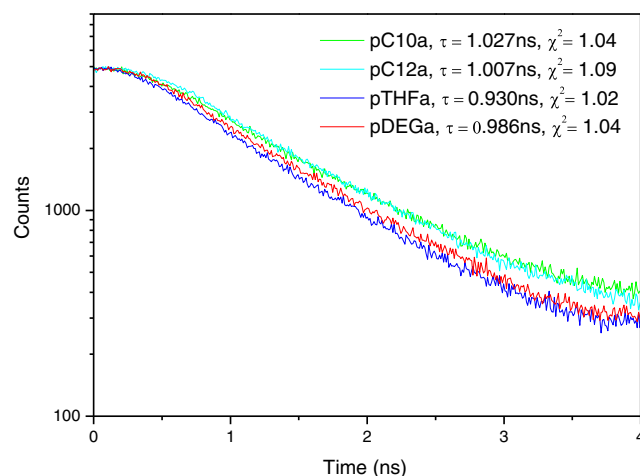
Table 2 Energy of the first singlet-excited state (E$_s$) and emission maxima (λ_{em}) of DBMBF$_2$ in four acrylic thin polymer films. Emission maxima (λ'_{em}) in monoliths

Polymer	E$_s$ (eV)	λ^1_{em} (nm)	λ^2_{em} (nm)	$\lambda^{1'}_{em}$ (nm)	$\lambda^{2'}_{em}$ (nm)
pC12a	3.16	392	411	398	414
pC10a	3.16	392	411	396	414
pTHFa	3.09	401	419	400	420
pDEGa	3.11	399	418	400	418

Fig. 3 Fluorescent lifetime of DBMBF$_2$ in 4 acrylic polymers: pC10a (green), pC12a (cyan), pDEGa (red), pTHFa (blue). The *legend* indicates the respective lifetimes and the goodness of fits
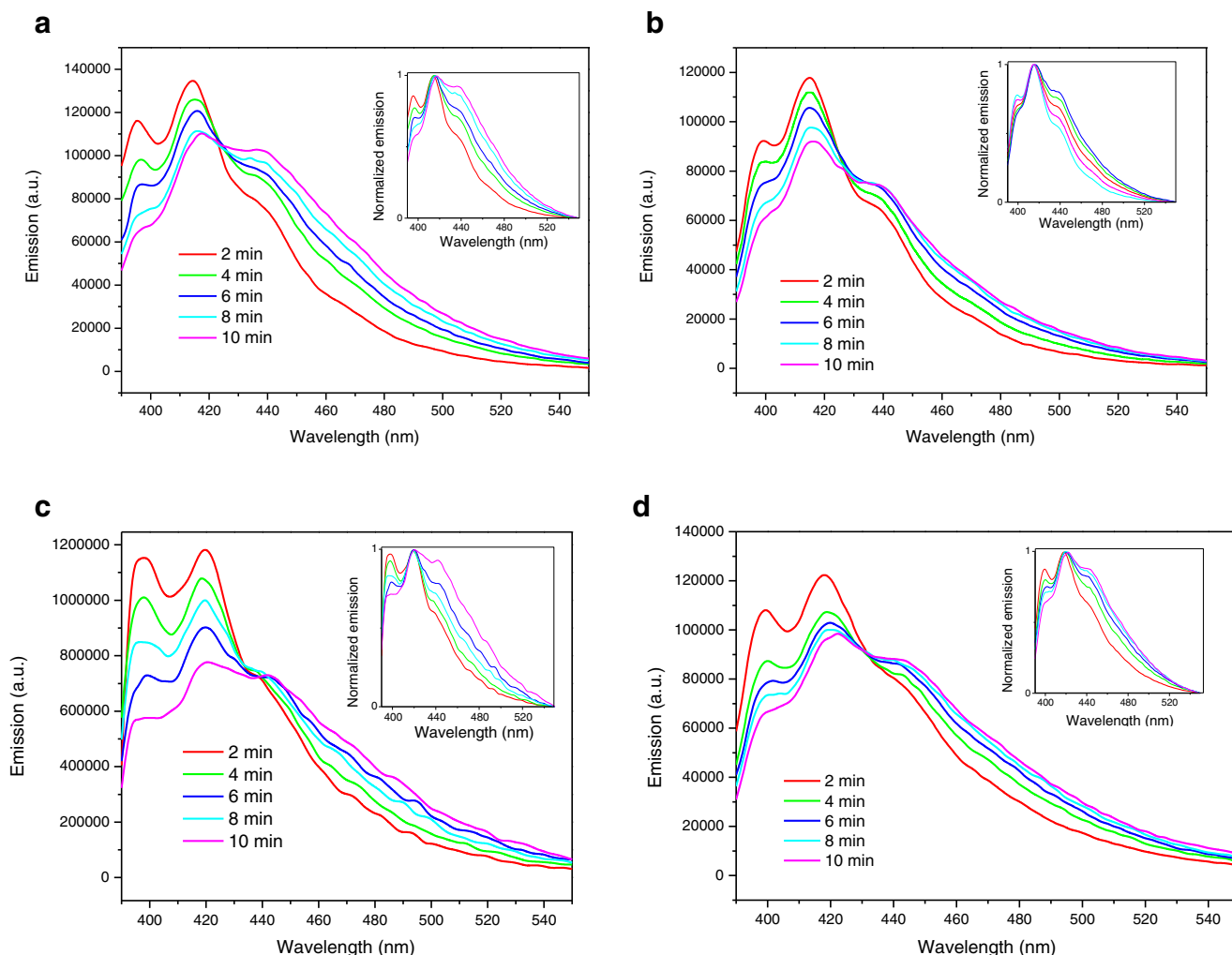
Legend: pC10a, $\tau = 1.027$ns, $\chi^2 = 1.04$; pC12a, $\tau = 1.007$ns, $\chi^2 = 1.09$; pTHFa, $\tau = 0.930$ns, $\chi^2 = 1.02$; pDEGa, $\tau = 0.986$ns, $\chi^2 = 1.04$

Fig. 4 Fluorescent response of DBMBF2 doped monoliths exposed to saturated toluene vapor with 2 min interval for **a** pC10a, **b** pC12a, **c** pTHFa, **d** pDEGa. The *insets* represent normalized fluorescent spectra curves

radiative rate of the dye in the polymers can be compared with the values in solution via the Strickler-Berg equation [34]. The equation relates k_R with the refractive index of the media, and it can be simplified and scaled to yield the relation between the values of k_R of dye in two different media, $k_{R,1}=(n_1/n_2)^2 * k_{R,2}$. For example using the value of the radiative rate in cyclohexane [14] ($k_{R,CH}$) of 0,33 ns and an average refractive index for the acrylates (~1.45) [35], the average k_R for the acrylate matrices obtained is 0,34 ns. The increment of k_R of the dye in the polymers indicates the non-radiative decay rate (k_{NR}) must have decreased. The reduction of k_{NR} is consistent with the increased viscosity of polymers compared to solution, which limits the movements of the excited dye within the matrix, reducing thermal or non-radiative deactivation mechanisms of the molecule. Similar behavior has been observed for measurements in solution at reduced temperatures [4]. The change of the quantum yield (ϕ) can be also estimated using the expression $\phi_1/\phi_2=k_{R,1}/k_{R,2} * \tau_{s,1}/\tau_{s,2}$. Using again the values reported for cyclohexane (ϕ_{CH}=0.046) [14] and an

average singlet lifetime of 1 ns for the doped polymers, the value obtained for the fluorescent quantum yield in the polymers is 0.32, representing almost a seventh-fold increase.

An interesting detail is the observed longer lifetimes for the dye in non-polar matrices compared to polar matrices. One would expect the stability of the excited state of a polar fluorophore such as DBMBF$_2$ to increases in more polar environments, and consequently result in an increase in fluorescence lifetime. This has been confirmed previously for the singlet lifetime of DBMBF$_2$, where an increase by a factor of three when changing from non-polar (n-hexane) to a polar (THF) solvent was reported [15]. In polymers matrices, similar behavior has been documented, in which polar dyes presented longer lifetimes in polymers with higher dielectric constants [36]. Other factors can be assigned to these lifetime changes, as rigidochromic effects [37, 38], reabsorption processes [39] or dye-dye interaction due to aggregation [21]. Rigidochromism can be discarded, as no correlation exists between the glass transition temperature (Table 1) of the
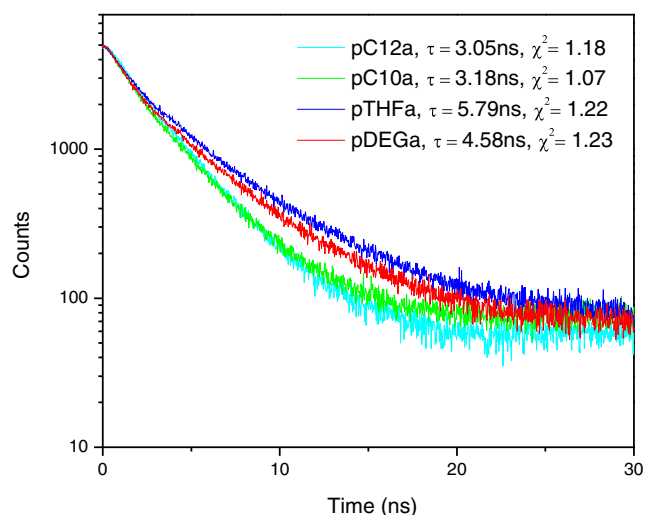
Fig. 5 Fluorescent lifetime of the DBMBF$_2$ exposed to toluene in pC12a (*cyan*), pC10a (*green*), pTHFa (*blue*), and pDEGa acrylate (*red*) matrix

polymers (indicator of the rigidity) and the fluorescent lifetime. Therefore some degree of aggregation in the non-polar matrixes is most likely responsible of the longer lifetimes.

Exciplex Formation with Toluene

The changes in fluorescence spectra of the DBMBF$_2$ doped polymer monoliths were measured when exposed to saturated toluene vapors (Fig. 4). As previously reported for DBMBF$_2$ in solution, adsorbed over porous silicas [17] or grafted to silica nanoparticles [18], the partial quenching of the original fluorescence, together with the appearance of the emission of a new exciplex species is observed. Our measurements show that the four polymers evaluated exhibit a similar phenomenon albeit with somewhat different spectral responses for the different matrices. The spectra are reported after 2 min of residence of the monolith within the saturated toluene vapors.

Spectra of unexposed samples showed small differences with spectra reported for t=2 min.

From the four polymers, the appearance of the exciplex band is most noticeable for the pC10a matrix. In all cases an isoemissive point is observed, which is typical for exciplex formation between the aromatic molecule and DBMBF$_2$ [13]. The position of the isoemissive point is found to be dependent on the polarity of the matrix, (pC10a: 423 nm, pC12a: 426 nm, pTHFa: 435 nm and pDEGa: 430 nm).

To obtain the exciplex spectra from the experimental data Alternating Least-Squares algorithm (ALS) [40] with non-negative and initial zero concentration of exciplex restrictions have been used. The obtained DBMBF$_2$ and exciplex spectra for the set of polymer are shown in Figure S1 (see *Supp. Info*). The maxima of exciplex spectra is shifted bathochromically with increasing polarity of polymer, according to well know equation for exciplex maxima [41].

The lifetimes of the exciplex show significant differences between the non-polar and polar matrices. The polar matrices exhibit longer fluorescent lifetimes (Fig. 5). In solution, after excitation, reorganization of the solvation shell occurs due to a change of dipole moment of the solute.

Compared to solution, polymers have a much higher viscosity, limiting and reducing molecular motion and reorganization. During the short lifetime of the singlet monomer emission with short emission lifetimes, the reorientation of the solvation shell is limited [39]. In contrast, the lifetime of the exciplex is long and allows a better reorganization of the polar polymeric chains and side groups around the excited polar species. The reorientation of the polar groups around the exciplex leads to stabilization of the species due to favorable dipole-dipole interactions. The stabilization reduces non-radiative decay mechanisms [42], leading to longer lifetimes of the exciplex.

Increasing the polarity of the medium favors the stabilization of the charge transfer state compared to the locally excited state, by increasing the resonance between the donor (aromatic
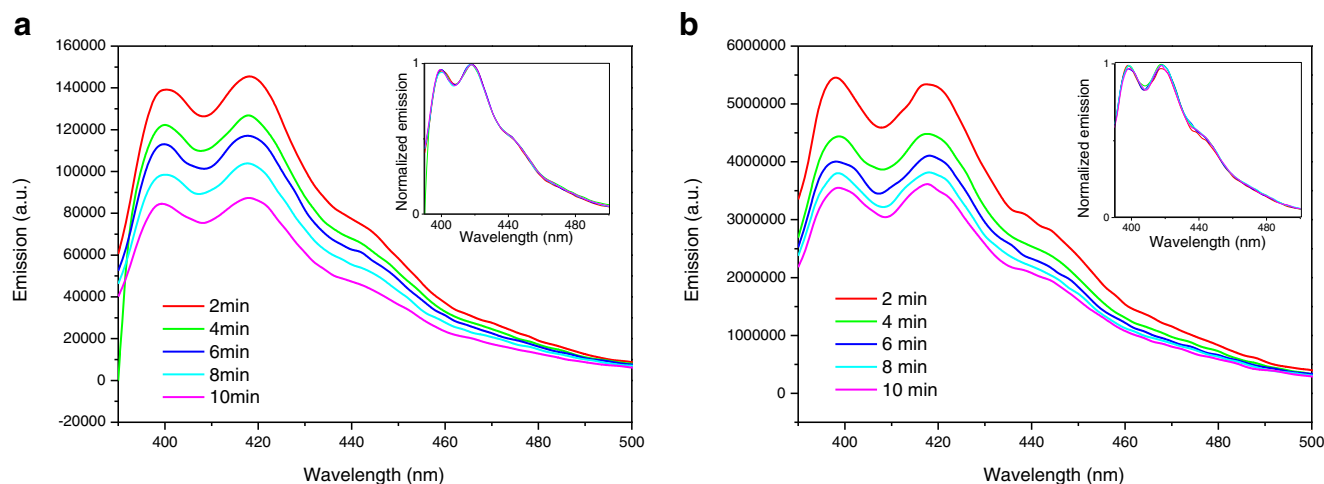

Fig. 6 Fluorescence behaviour of DBMBF$_2$-doped pTHFa to non-aromatic gases: **a** Response towards n-hexane, **b** Response towards ethanol

molecule) and the acceptor (excited fluorophore) [43, 44]. The exciplex formed with toluene has a high charge transfer component (~51 %) [13], therefore more susceptible to the stabilization effects from the environment. The increased polarity of pTHFa could lead to the formation of solvent shared ion pair (SSIP) [30, 43]. The SSIP formation can reduce the fluorescent yield of the exciplex and its radiative decay rate (k_R) [43]. The reduction of k_R could further explain the longer exciplex lifetime observed in pTHFa in Fig. 5.

Fluorescent Behavior with Non-Aromatic Compounds

The evolution of the fluorescence spectra of DBMBF$_2$ doped pTHFa and pC12a over time to the exposure of saturated nonpolar n-hexane and polar ethanol was monitored in Fig. 6. A reduction of the total fluorescence occurs, without the appearance of a new emission band. This can be directly seen from the normalized spectra in the inset of Fig. 6. The same was observed for pDEGa, pC10a and pC12a (see Fig. S3 in *Supp. Info.*). No isoemissive points were found for any of the spectra and the reduction of the fluorescence was found to be reversible after removal of the monolith from the saturated vapor. The decrease in the fluorescence under exposure to hexane and ethanol is related to a reduction in the quantum yield of the fluorophore and by changes in refractive indexes. The reduction in quantum yield is a consequence of an increase in non-radiative decay mechanisms due to specific or nonspecific fluorophore-solvent interaction [45]. For ethanol vapors, hydrogen-bonding interactions with the fluorophore is the most likely mechanism for an increase of internal conversion relaxation mechanisms, which reduces the fluorescence quantum yield. In the case of hexane, non-specific interactions are most likely responsible for the fluorescent reduction. The absorption of hexane by the polymers can lead to swelling of the polymer and an overall increment of translational and vibrational freedom of the polymer. The reduction of the rigidity of the polymer is then observed as reduced fluorescence of the dye [19, 46, 47]. The absence of additional fluorescent bands or red-shifts under exposure to polar as well as nonpolar compounds is highly desirable for the development of a selective gas sensor.

Conclusion

Thin layers and monoliths of polymers doped with DBMBF$_2$ were successfully prepared, showing no or reduced aggregation of the dye. The excitation and fluorescent spectra in combination with gas response behavior of the doped polymers were studied by fluorescence spectroscopy and time-resolved florescent lifetime measurements. The formation of a fluorescent exciplex was successfully observed when exposing the

materials to toluene. While for hexane and ethanol only reduction of the fluorescence occurred. These results confirm the potential of polymers doped with DBMBF$_2$ for the selective detection of MAHs. The observation of exciplex in polymers with a very varied chemistry opens the possibilities of further tuning the matrix composition to enhance the response, selectivity and sensitivity of such polymers. Furthermore, the immobilization of the dye in polymers significantly increases the quantum yield enhancing the intensity of fluorescence that can be detected from the doped polymers. Similar to the phenomena observed in solution, the polarity of the polymer shows influence on excitation, emission maxima and lifetime of the dye. These are effects that could be exploited when considering the design or read-out of fluorescent sensor.

In summary, the analysis and results of this study show that acrylic matrices doped with DBMBF$_2$ are a promising class of materials for the development of selective and reversible fluorescent sensors for monocyclic aromatic compounds.

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