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Convenient tautomeric forms in an amino-anthraquinone diimine for the generation of a mixed-valent push–pull conjugated polymer†

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The use of NH_2 on the $(Pt(C{\equiv}C)_2(PBu_3)_2)_n$/anthraquinone diimine$)_n$ polymer induces a tautomeric species which leads to a mixed-valent form reminiscent of emaraldine in polyaniline.

Polyaniline (PANI) is a redox active π-conjugated 1D material exhibiting applications in anticorrosive coatings, solar energy conversion, electronic devices, rechargeable batteries, artificial muscles and sensors.[1,2] It exists under three different redox forms: the fully reduced leucoemeraldine, the fully oxidised perigraniline, and the mixed-valent emeraldine (Fig. 1).[2] Emaraldine becomes a conductive polymer when protonated.

In parallel, platinum(II)polyyne-containing polymers are subjects of current and intense interest as they offer the possibility of low-band gap excited states and many studies on their bulk hetero-junction solar cells have been reported.[3] Similarly, these materials are also found to be electroluminescent and light emitting diodes were studied.[4] Recently, our group explored the quinone diimine-containing conjugated polymers **1–4** where the push–pull process is defined by the donor ability of the *trans*-$Pt(PR_3)_2$ units and the acceptor properties of the quinone substituents X (Fig. 2).[5]

1–3 are the oxidized version, whereas **4** is the mixed-valent form. The synthesis of the latter requires the mixing of both the reduced and oxidized precursors prior to polymerization,[5c] leading to an irregular sequence of oxidized and reduced units in the chain. We report herein an original way to produce the mixed-valent form (**6**) using a unique precursor, amino-anthraquinone (**7b**), taking advantage of the formation of a tautomeric form. Its detection is made using ^1H NMR, IR and emission spectroscopy.

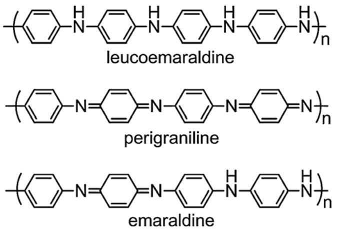


Fig. 1 The three different redox forms of PANI.

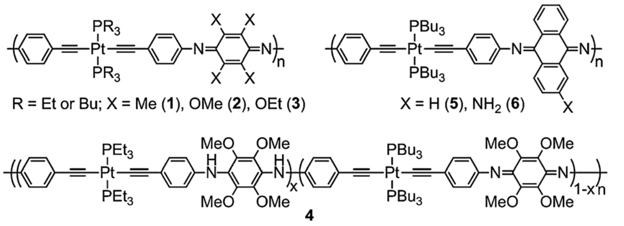
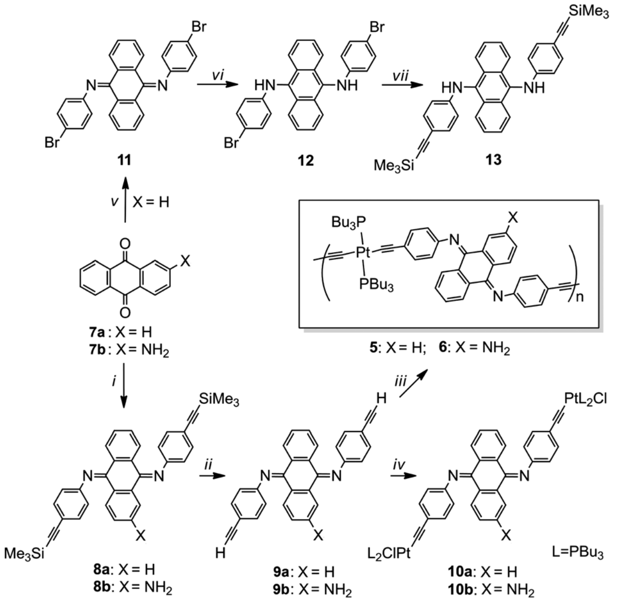


Fig. 2 Structures of the quinone diimine-containing polymers.

The fully oxidized **5** and **6** are prepared in three steps from the commercially available **7a**,**b** and *p*-$Me_3SiC{\equiv}CC_6H_4NH_2$ (Scheme 1; see Experimental section in the ESI†). **8a**,**b** are prepared from **7a**,**b** using a condensation method with $TiCl_4$ which are then deprotected using a weak base (K_2CO_3) to



i) 2 p-$Me_3SiCCC_6H_4NH_2$, $TiCl_4$, Et_3N, PhCl, 60°C, 4hrs; *ii)* K_2CO_3, MeOH/THF; *iii)* 1 eq. *trans*-$PtCl_2(PBu_3)_2$, CuI, i-Pr_2NH,CH_2Cl_2; *iv)* 7eq. *trans*-$PtCl_2(PBu_3)_2$, CuI, i-Pr_2NH,CH_2Cl_2; *v)* 2 p-$NH_2C_6H_4Br$, $TiCl_4$, Et_3N, PhCl, 60°C, 4hrs; *vi)* HI, CH_2Cl_2; *vii)* Me_3SiCCH, $PdCl_2(PPh_3)_2$,PPh_3, CuI,i-Pr_2NH,PhMe, 60°C.

Scheme 1 Synthesis of **5**, **6**, **10a**,**b** and **13**.

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Table 1 Gel permeation chromatography data for **5** and **6**

Polymer	M_n	nb. of units	M_w	PD
5	15 200	14.6	25 800	1.70
6	18 100	17.2	51 400	2.93

form **9a**,**b**. The characterization is performed by ^{1}H NMR, IR (ν(C$\equiv$C), ν(C=N), ν(N–H)), mass spectrometry (EI) and chemical analysis. The X-ray structure of **8a** was also determined (ESI†), which reveals the common butterfly structure.[6] **9a**,**b** react with 1 or 7 eq. of *trans*-$PtCl_2(PBu_3)_2$ in the presence of CuI and *i*Pr_2NH to respectively form **5** and **6**, or models **10a**,**b**. GPC, (gel permeation chromatography; Table 1) reveals an oligomeric nature of ~14 to 17 units for the polymers. The $^1J(^{31}P–^{195}Pt)$ coupling constants of 2352–2383 Hz in the ^{31}P NMR spectra confirm the *trans*-geometry about the Pt atom.[5b] A fully reduced model, **13**, is prepared in three steps from **7a**, which was first coupled with *p*-$BrC_6H_4NH_2$ to afford **11**. The latter is then reduced with HI to form **12**, which is then coupled with $Me_3C\equiv CH$ to form **13** confirmed by X-ray crystallography (ESI†).

The UV-vis spectra of the fully oxidized species **8a**, **10a**, and **5** exhibit the characteristic low energy charge transfer (CT) band $C\equiv CC_6H_4$ → quinone (ESI†).[5] The position and absorptivity data (see **5** in Table 2) compare well with that of the poly(anthraquinone diimine phenylene) material (λ_{max} = 468 nm; ε = 6200 M^{-1} cm^{-1}).[7] The high energy bands in the 300–350 nm window stem from the $C\equiv CC_6H_4$ $\pi \rightarrow \pi^*$ transitions. The emission properties of **8a**, **10a**, and **5** (ESI†) were studied at 77 K since they are not luminescent at 298 K. They exhibit the fluorescence (ns) and phosphorescence (µs) bands arising from the $\pi\pi^*$ manifolds of the $C\equiv CC_6H_4$ unit (*i.e.* $S_2 \rightarrow S_0$ and $T_2 \rightarrow S_0$), not from the CT ones.[5] These are used as fingerprint for the presence of the oxidized moiety. Indeed, the mono-amino-anthraquinone diimine-containing models **8b** and **10b** exhibit the expected structured $S_2 \rightarrow S_0$ fluorescence and $T_2 \rightarrow S_0$ phosphorescence associated with the $C\equiv CC_6H_4$ unit (Fig. 3; red traces). However, a new emission at ~535 nm is detected. A fluorescence of the CT excited state (*i.e.* $S_1 \rightarrow S_0$) was first suspected due to its apparent proximity with the CT band (Stoke shift: ~4700 (**8b**), ~3500 cm^{-1} (**10b**)) and is short lifetime (*i.e.* τ_F; ns time scale; the photophysical detail is in the ESI†). As the relative emission intensity depends on λ_{exc} (*i.e.* the maxima of the excitation lowest energy band does not match well the absorption one, neither in position as in **8b** nor in bandwidth as in **10b**) another species is therefore responsible for the extra emission at ~535 nm. Its identification is readily made using the fully reduced model **13**, which exhibits an unstructured fluorescence at ~510 nm (Stoke shift = 2600 cm^{-1}; τ_F = 6.09 ± 0.09 ns).

13, **8b**, and **10b** were also studied at 298 K (Fig. 4) and the same comments described above apply. No phosphorescence is noted leaving only the fluorescence appearing in the spectra, notably the ~535 nm signal common to **13**, **8b**, and **10b**.

Table 2 Absorption data for **5** and **6** in 2MeTHF at 298 K

Polymer	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	ε (M^{-1} cm^{-1})
5	295	15 700	449	4230
6	290	14 400	428	6600

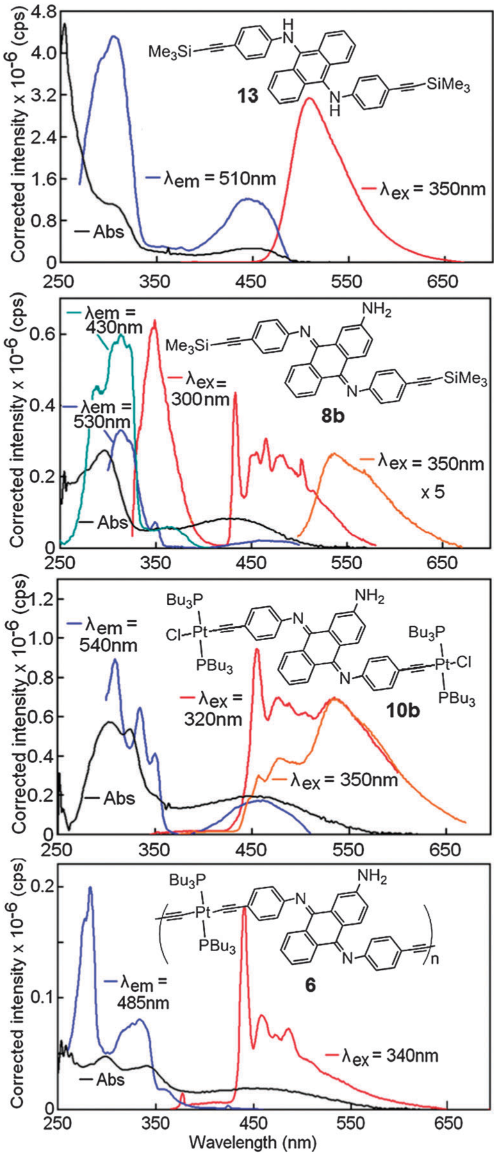

Fig. 3 Absorption (black), fluorescence (red, orange), and excitation (blue, turquoise) spectra of **13**, **8b**, **10b** and **6** in 2MeTHF at 77 K.

The τ_F data for this signal are 4.52 ± 0.06 (**13**), 4.49 ± 0.05 (**8b**), and 4.64 ± 0.02 ns (**10b**). The similarity in λ_{max} and τ_F provides a strong proof that the ~535 nm emission is the fluorescence arising from an amine unit. The absence of heavy atom effect on the fluorescence (τ_F should decrease when Pt is introduced) is explained by the long Pt/amine-containing chromophore distance. The possibility of the anthraquinone diimine fragment be reduced into 1,4-diamino-benzene during the synthesis is ruled out since under the same conditions **8a**, **10a** and **5** were never reduced. Consequently, the presence of these two emissions is due to tautomers (Fig. 5). Tautomerism in anthraquinone imines and anthraquinones is indeed well known.[8] Forms A and B must co-exist in the ground state since they are both detected at 77 K and long range proton transfer is most unlikely to occur in frozen media. The presence of tautomers is evidenced by the presence of two ^{1}H NMR N$\underline{H}$ resonances at ~4 ppm (**8b** and **10b**) and by three IR signals in the 3220–3475 cm^{-1} window (**8b**, **9b**, **10b** and **6**; detail in ESI†)

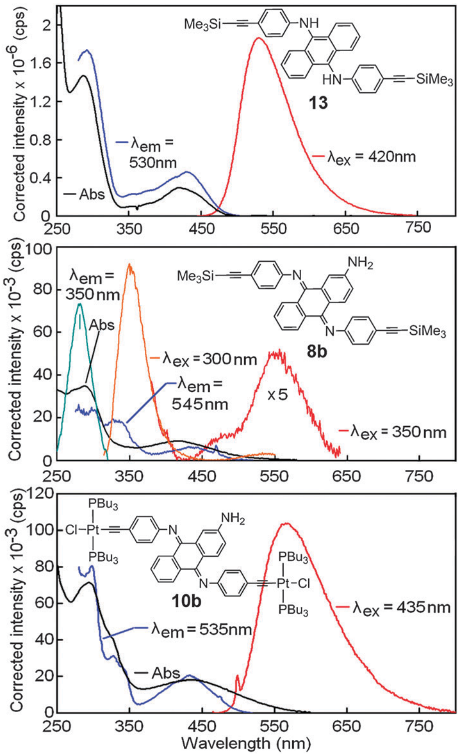

Fig. 4 Absorption (black; arbitrary units), fluorescence (red, orange), and excitation (blue, turquoise) spectra of **13**, **8b**, and **10b** in 2MeTHF at 298 K. The shoulder at ~480 nm (red trace in **8b**) is due to an impurity.

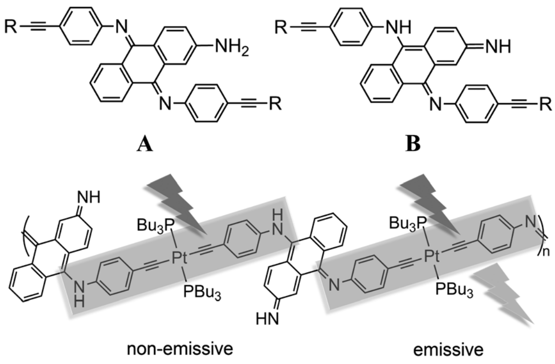

Fig. 5 Top: Tautomer forms in **8b**, **10b** and **6**. Bottom: structure of a fragment of the mixed-valent amine–imine polymer **6** (not necessarily alternated) stressing its emission behaviour at 77 K.

whereas only one (^{1}H NMR) and two (IR) signals are expected for form A.

No fluorescence arising from the amino-benzene unit at ~535 nm is confidently observed in **6** at 298 and 77 K, although a shoulder at this position is noted at 77 K (Fig. 4). The absence or weakness of this signal does not exclude the possibility of tautomeric forms as **10b** exhibits a strong amino-benzene fluorescence and that the IR spectra of **6** exhibit the same fingerprint as those measured for **8b**, **9b** and **10b**. Attempts to prepare the corresponding fully reduced model complex and polymer from **13** stubbornly failed for unknown reasons. The resulting materials were always the fully oxidized polymer **6** and complex **10b**. Therefore, this tautomer property now appears to be an appealing alternative to prepare a polymer exhibiting features approaching that of the reduced form of **5**. Indeed, the tautomeric form B of **6** (Fig. 5) contains both imine and amine units along the polymer chain, so it exists as a mixed-valent polymer, similar to the organometallic version of PANI illustrated in Fig. 1 (**4**). To the best of our knowledge, this strategy has never been used for organic PANI and its analogues and may open the door to new developments in functional polymers.

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