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Profound Substituent Effect on the Structural, Optical, Photophysical, and Electrochemical Properties of N,N'-Anthraquinone Diimine-Containing Platinum–Organometallic Polymers

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Supporting Information

ABSTRACT: A series of conjugated organometallic-substituted derivatives of anthraquinone diimine-(*trans*-diethynylbis-(tri-*n*-butylphosphine)platinum(II)-containing polymers along with the corresponding mixed-valence analogues bis(4-phenylamino)anthracene and anthraquinone diimine and model compounds (substituent = H, Br, 2Br, NH₂, 2NH₂) were investigated by electrochemistry, UV-visible and emission spectroscopy, photophysics, and DFT and TDDFT computations, as a means to shine light on the electronic communication across the chain of the seemingly unconjugated polyaniline in its emeraldine form and to examine the substituent effect.

INTRODUCTION

Polyaniline (PANI) exists as its reduced (leucoemeraldine), oxidized (perigraniline), and mixed-valent forms (emeraldine; Chart 1), and its derivatives exhibit interesting features for the design of electrochemical sensors, rechargeable batteries, organic light emitting diodes (OLEDs), and solar cells.¹ Recently, PANI received substantial attention as an "ingredient" for the construction of photovoltaic cells, notably dye-sensitized solar cells (DSSCs).² Some success in these designs was also obtained by covalently attaching metal complexes onto a conjugated polymer mixed with sulfonated PANI³ and using small-size (1.5 nm) and 1-D nanoparticles of platinum as a composite.⁴

Concurrently, the *trans*-bis(ethynylaryl)bis(phosphine)platinum(II) unit, [**Pt**], inserted within the skeleton of conjugated polymers was also made, aiming at potential solar cell applications.⁵ The structural similarity of perigraniline and emeraldine with the N,N'-quinone diimine-containing Ptorganometallic polymers **P1a**-**e**, ([**Pt**]-**Q**)_n (**Q** = quinone diimine), as well as the charge transfer (CT) spectral signature giving the PANI's bluish coloration, was readily noted.⁶ Unsurprisingly, the optical and redox properties turned out to be both strongly geometry^{6a} and substituent dependent.^{6b,7} One key feature is the long-standing stability of these [**Pt**] materials (i.e., years) without losing their luminescence and redox properties, which makes them extremely appealing.⁶

Recently, the connectivity effect was also tested by branching the **Q** unit with [**Pt**] via a NMe bridge at the α -positions, hence rendering polymer **P2** unconjugated (Chart 1).⁸ Unexpectedly, the CT interaction between the electron-rich [**Pt**] and -poor **Q**



moieties was still present in the same way as observed for P1a– e, indicating that the NMe bridge secures the electronic communication between the units despite the lack of conjugation. These findings gave a valuable clue on the nature of the electronic communication across the seemingly unconjugated emeraldine form of PANI. Attempts to prepare the corresponding fully reduced Pt–organometallic leucoemeraldine version (i.e., $([Pt]-NR-C_6X_4-NR)_n, R = H, X = OMe,$ Me, H, F, Cl) turned out to be very difficult, where, at best, both oxidized and reduced units were found in the chain.^{6,7}

During the course of this study, the anthraquinone diimine residues, AQ, were also used, where two brief preliminary accounts were reported on polymers P3a-e (Chart 1) and two unexpected observations were made.^{9,10} First, the CT bands issuing from the [Pt] residue to the AQ moiety in P3a-c,e were notably blue-shifted with respect to the Q-containing polymers P1a-e despite the extended conjugation in the AQ unit. Similarly, the reduction waves recorded by cyclic voltammetry are shifted to more negative potentials. This phenomenon was tentatively attributed to the butterfly structure of AQ (instead of planar) induced by steric hindrance of the 1,4,5,8-H atoms with the [Pt]-phenyl groups.⁹ This effect renders attempts to establish a structure-property relationship difficult. Second, when the electron-donating group NH₂ is used at the 2-position (providing P3d), evidence for the presence of a mixture of "static" tautomeric forms was made by ¹H NMR, IR, and fluorescence spectroscopy, where the imine

Received: February 19, 2015 Published: April 8, 2015 Chart 1. List of Polymers Discussed or Investigated in This Work^a



^aThe gray areas represent the structural differences between perigraniline-, emeraldine-, and the quinone-containing Pt polymers.

function can be placed at either the N- or 2-positions in the polymer backbone.¹⁰ This finding provides a very convenient "one-pot" method for the introduction of reduced quinone residues in the skeleton of the conjugated polymer containing the oxidized **AQs**. Unfortunately, this approach does not allow for a strategy controlling the relative ratio of reduced/oxidized **Q** or **AQ** in the chain.

We now report a more complete account on the physical, electrochemical, optical, and photophysical properties of the oxidized polymers P3a-e and mixed-valence ones P5a-d (Chart 1) along with their corresponding models (Chart 2). The observations are analyzed through DFT and TDDFT calculations (B3LYP; 3-21G* basis sets). Profound changes in properties are found upon the change in substitution on AQ (2 Br, Br, H, NH₂, 2 NH₂). The key features focus on the tautomeric form descriptions and the particularly drastic changes in photophysical properties upon substitution. Moreover, the syntheses of the corresponding Pt-organometallic version of leucoemeraldine, ([Pt]-NH-anthracene-NH), and the model complexes ClPt(PBu₃)₂-NH-anthracene-NH-Pt- $(PBu_3)_2$ Cl remain elusive. At best, mixed-valence version polymers $(([Pt]-AQ)_{r}([Pt]-NH-anthracene-NH)_{v})_{r}$ were successfully prepared. Moreover, in light of the recent observation that electronic communication between two unconjugated units across a polymer chain (i.e., in P2) is secured by an NR bridge (R = H, Me)⁸ the newly prepared aryl-NH-anthracene-NHaryl (aryl is defined in Chart 2) and mixed-valence [Pt]containing polymers provide further evidence for this trend

despite the unfavorable dihedral angle between the anthracene and aryl planes.

EXPERIMENTAL SECTION

Materials. Compounds 1a–c, 2a–d, 3a–d, polymers P3a–d, and *trans*-Pt(PBu₃)₂Cl₂ were prepared according to literature procedures.^{7,9,11–14} Sodium tetrahydroborate, hydroiodic acid, zinc dust, NH₄Cl, and K₂CO₃ were purchased from Aldrich and were used as received. All reactions were performed in Schlenk-tube flasks under argon. All flasks were dried under a flame to eliminate moisture. All solvents were distilled from appropriate drying agents.

N,N'-Bis(*para*-bromophenyl)-9,9'-diaminoanthracene (5a). A 0.90 g amount of 1a (1.7 mmol) was dissolved in 50 mL of CH_2Cl_2 . Then 0.78 mL (4.3 mmol) of a 40% HI solution was added dropwise into a stirred solution of 1a in CH_2Cl_2 . The solution was allowed to stir for 30 min at room temperature. The reaction mixture was filtered through a fine glass sintered funnel, evaporated, and purified on a silica column with CH_2Cl_2/THF (2:1, v/v) as the solvent to give the diamine compound 5a. Yield: 0.55 g (61%). IR (KBr)/cm⁻¹: 3386 (N–H). ¹H NMR (CDCl₃): δ 8.19 (4H, m, CH arom.), 7.46 (4H, m, CH arom.), 7.24 (4H, d, CH arom., J = 8.7) 6.48 (4H, d, CH arom., J = 8.7), 6.05 (2H, s, -NH) ppm. MS: m/z (EI) 518 (M⁺).

N,*N*'-Bis(*para*-bromophenyl)-9,9'-diamino-2-bromoanthracene (5b). 1b (297.5 mg, 0.5 mmol) was added to 50 mL of THF/ ETOH (1:1 v/v). NaBH₄ (76 mg, 2 mmol) was added. The solution was stirred at room temperature for 3 h. Then 50 mL of water was added, and all solvents were removed under vacuum after stirring for 10 min. The crude product was purified by column chromatography using CH₂Cl₂/THF (2:1, v/v) as the eluent to give the yellow compound **Sb** (250 mg, 84%). IR (KBr)/cm⁻¹: 3382 (N–H). ¹H NMR (300 MHz, CDCl₃): δ 8.38 (s, 1H, Ar), 8.20 (m, 4H, Ar), 8.17 (d, *J* = 3 Hz, 1H, Ar), 8.07 (d, *J* = 9 Hz, 4H, Ar), 7.23(d, *J* = 3 Hz, 2H,



Ar), 6.48 (t, J = 9, 3 Hz, 4H, Ar), 5.90 (br, 2H, 2N–H) ppm. ESI-Tof: m/z calculated 618.8815 (MNa⁺), m/z observed 618.8826 (MNa⁺).

N,*N*'-Bis(*para*-ethynylphenyl)-9,9'-diamino-2,2'-dibromoanthracene (5c). 1b (674 mg, 1 mmol) was added to 50 mL of THF/ ETOH (1:1 v/v). NaBH₄ (152 mg, 4 mmol) was added, and the solution was stirred at room temperature for 3 h. Then 50 mL of water was added, and all solvents were removed under vacuum after stirring for 10 min. The crude product was purified by column chromatography using CH₂Cl₂/THF (2:1, v/v) as the eluent to give the yellow compound 5c (642 mg, 95%). IR (KBr)/cm⁻¹: 3391 (N– H), 1591, 1485 cm⁻¹. ¹H NMR (CDCl₃): δ 8.36 (2H, s, CH arom.), 8.04 (1H, s, CH arom.), 8.02 (1H, s, CH arom.), 7.56–7.53 (4H, m, CH arom.) 6.47 (4H, s, CH arom.), 6.45 (3H, s, CH arom.), 3.37 (2H, s, –NH) ppm. MS: *m*/*z* (ESI-TOF) 676.8077 (MH⁺).

N,*N*′-**Bis**(*para*-ethynylphenyl)-9,9′-diaminoanthracene (5d). 3a (81.3 mg, 0.2 mmol) was added to 50 mL of THF, and Zn dust (52.3 mg, 0.8 mmol) and NH₄Cl (171.2 mg, 3.2 mmol) were added. The solution was refluxed for 5 h. After filtration, the crude product was purified by column chromatography using CH₂Cl₂/hexanes (2:1, v/v) as the eluent to give the yellow compound 5d (75 mg, 92%). IR (KBr)/cm⁻¹: 3387, 3285 (N−H), 2097 (C≡CH). ¹H NMR (300 MHz, CDCl₃): δ 8.20 (q, *J* = 3.3 Hz, 4H, Ar), 7.48 (q, *J* = 9 Hz, 4H, Ar), 7.30 (d, *J* = 8.7 Hz, 4H, Ar), 6.53 (d, *J* = 8.7 Hz, 4H, Ar), 6.14 (s, 2H, 2NH), 2.96 (s, 2H, C≡CH). ¹³C NMR (CDCl₃): δ 148.46, 133.74, 130.97, 129.90, 126.57, 124.34, 113.65, 111.75, 84.46, 75.30. MS: *m*/*z* calculated 409.1699 (MH⁺), *m*/*z* observed 409.1731 (MH⁺).

Polymer P5a. P3a (152 mg, 0.01 mmol) was added to 50 mL of THF under Ar, and Zn dust (37.9 mg, 0.58 mmol) and NH_4Cl (125.2 mg, 2.34 mmol) were added. The solution was refluxed for 2 h. After filtration, the crude product was purified by column chromatography using CH_2Cl_2 /hexanes (2:1, v/v) as the eluent to give the orange

material **P5a** (138.3 mg, 91%), stored under Ar. IR (KBr)/cm⁻¹: 3392, 3310 (N–H), 2102 (C=CH). ¹H NMR (300 MHz, CDCl₃): δ 8.22 (br, 4H, Ar), 7.44 (br, 4H, Ar), 7.06 (br, 4H, Ar), 6.80 (br, 1H, N–H) 6.48 (br, 4H, Ar), 5.97 (br, 1H, N–H), 2.11 (b, 12H, 6PCH₂C₃H₇), 1.58 (b, 12H, 6PCH₂CH₂C₂L₅), 1.45–1.36 (m, 12H, 6PCH₂CH₂CH₃), 0.95–0.86 (m, 18H, 6PCH₂CH₂CH₂CH₂CH₃) ppm. ³¹P NMR (122 MHz, CDCl₃): δ 2.59 (¹J_{P-Pt} = 2383 Hz). Anal. Found: C, 65.59; H, 6.98; N, 2.53. (C₁₀₉H₁₄₆N₄P₄Pt₂)_n requires: C, 64.61; H, 7.26; N, 2.76.

Polymers P5b-d were prepared in the same way as described for P5a above.

Polymer P5b (89%). IR (KBr)/cm⁻¹: 3382, 3309 (N–H), 2105 (C≡CH). ¹H NMR (300 MHz, CDCl₃): δ 8.21 (br, 4H, Ar), 7.49 (br, 3H, Ar), 7.11 (br, 3H, Ar), 6.53 (br, 5H, Ar), 5.15 (br, 2H, N–H) 2.07 (b, 12H, $6PCH_2C_3H_7$), 1.71 (b, 12H, $6PCH_2CH_2C_1H_5$), 1.44 (m, 12H, $6PCH_2CH_2CH_2CH_3$), 0.92 (m, 18H, $6PCH_2CH_2CH_2CH_3$) ppm. ³¹P NMR (122 MHz, CDCl₃): δ 2.65 (¹ J_{P-Pt} = 2384 Hz). Anal. Found: C, 61.28; H, 7.03; N, 2.27. (C₁₀₉H₁₄₄Br₂N₄P₄Pt₂)_n requires: C, 59.94; H, 6.65; N, 2.57.

Polymer P5c (90%). IR (KBr)/cm⁻¹: 3385, 3310 (N–H), 2110 (C≡CH). ¹H NMR (300 MHz, CDCl₃): δ 8.37 (br, 2H, Ar), 8.03 (br, 2H, Ar), 7.48 (br, 2H, Ar), 7.29 (br, 2H, Ar), 7.10 (br, 2H, Ar), 6.46 (br, 4H, Ar), 5.85 (br, 2H, N–H), 2.13 (b, 12H, 6PCH₂C₃H₇), 1.59 (b, 12H, 6PCH₂CL₂C₂H₅), 1.45 (m, 12H, 6PCH₂CH₂CH₂C), 0.92 (m, 18H, 6 PCH₂CH₂CH₂CH₂CH₃) ppm. ³¹P NMR (122 MHz, CDCl₃): δ 2.66 (¹J_{P-Pt} = 2382 Hz). Anal. Found: C, 56.33; H, 6.49; N, 2.19. (C₁₀₉H₁₄₂Br₄N₄P₄Pt₂)_n requires: C, 55.90; H, 6.11; N, 2.39.

Polymer P5d (91%). IR (KBr)/cm⁻¹: 3390, 3310 (N–H), 2105 (C≡CH). ¹H NMR (300 MHz, CDCl₃): δ 8.06 (br, 6H, Ar), 7.09 (br, 6H, Ar), 6.50 (br, 3H, Ar), 3.77(br, 2H, N–H), 3.17 (s, 1H, terminal C≡CH), 2.98 (s, 1H, terminal C≡CH), 2.11 (b, 12H, $6PCH_2C_3H_7$), 1.57 (b, 12H, $6PCH_2CH_2C_2H_5$), 1.45–1.36 (m, 12H, $6PCH_2CH_2CH_2CH_3$), 0.91 (m, 18H, $6PCH_2CH_2CH_2CH_3$) ppm. ³¹P NMR (122 MHz, CDCl₃): δ 2.56 (¹J_{P-Pt} = 2388 Hz). Anal. Found: C, 64.31; H, 7.64; N, 3.68. (C₁₀₉H₁₄₈N₆P₄Pt₂)_n requires: C, 63.66; H, 7.25; N, 4.09.

X-ray Crystallography. The crystals of 5a were grown by slow evaporation of a CH₂Cl₂ solution. One single crystal (0.05 \times 0.20 \times 0.60 mm³) was mounted using a glass fiber on the goniometer. The crystals of 5b were grown by slow evaporation of a CHCl₃ solution at room temperature. One single crystal $(0.05 \times 0.15 \times 0.80 \text{ mm}^3)$ was mounted using a glass fiber at 293(2) K on the goniometer. In both cases, data were collected on an Enraf-Nonius CAD-4 automatic diffractometer using omega scans at 293(2) K. The DIFRAC¹⁵ program was used for centering, indexing, and data collection. One standard reflection was measured every 100 reflections, and no intensity decay was observed during the data collection. The data were corrected for absorption by empirical methods based on φ scans and reduced with the NRCVAX¹⁶ programs. They were solved using SHELXS-97¹⁷ and refined by full-matrix least-squares on F^2 with SHELXL-97.18 The non-hydrogen atoms were refined anisotropically. For 5a, the H atoms were placed at idealized calculated geometric positions using a riding model, except for H10 and H13, which were found by Fourier differences. They were all isotropically refined. For 5b, the hydrogen atoms were also placed at idealized calculated geometric positions and refined isotropically using a riding model. The bromine atom sitting on the anthraquinone is disordered over two geometric equivalent sites. For this reason, the occupation is 50% on each opposite side.

Instruments. The ¹H, ¹³C, and ³¹P NMR spectra were collected on a Bruker DRX 300 and 400 spectrometer in CDCl₃ solution with tetramethylsilane as internal standard. All chemical shifts (δ) and coupling constants (J) are respectively given in ppm and Hz. The IR spectra were acquired on a Bomem FT-IR MB series spectrometer equipped with a baseline-diffused reflectance. EI-MS were recorded on a LCQ DECA XP liquid chromatograph—mass spectrometer (Thermo Group). TGA were acquired on a PerkinElmer TGA 7 between 50 and 950 °C at 3 °C/min under a nitrogen atmosphere. The UV/vis spectra were recorded on a Hewlett-Packard diode array model 8452A. The emission and excitation spectra were obtained by using a double Scheme 1^a



^{*a*}Conditions: (i) HI 40%, CH₂Cl₂, 30 min. (i') NaBH₄, THF/EtOH. (ii) K₂CO₃, MeOH/THF (1:1), 12 h. (iii) Zn dust, NH₄Cl, THF, 5 h. (iv) 1 equiv of *trans*-PtCl₂(PBu₃)₂, CuI, *i*Pr₂NH, CH₂Cl₂. (v) Zn dust, NH₄Cl, THF, 3 h (a: X = X' = H; b: X = H, x' = Br; c: X = X' = Br; d: X = H, $X = NH_2$).

monochromator Fluorolog 2 instrument from Spex (Horiba). Phosphorescence and fluorescence lifetimes were measured on a Timemaster model TM-3/2003 apparatus (PTI). The source was a N₂ laser with a high-resolution dye laser (fwhm \approx 1.5 ns), and the fluorescence lifetimes were obtained from high-quality decays and deconvolution or distribution lifetime analysis. The uncertainties were ~40 ps based on multiple measurements, although the reliability on the measurements is 100 ps. The phosphorescence lifetimes were also performed on a PTI LS-100 using a 1 μ s tungsten flash lamp (fwhm ~1 μ s).

Quantum Yield Measurements. All samples were prepared under argon (in a glovebox, $O_2 < 12$ ppm) by dissolution of the compounds in 2MeTHF using 1 cm³ quartz cells with a septum, for the 298 K measurements. Three different measurements (different solutions) were performed for each set of quantum yields. The sample concentrations were chosen to correspond to an absorbance of 0.05 at the excitation wavelength. Each absorbance was measured five times for better accuracy in the measurements of emission quantum yield. The reference was 9,10-diphenylanthracene ($\Phi_{\rm F} = 1.0$).¹⁹

Theoretical Calculations. Calculations were performed with Gaussian 09²⁰ at the Université de Sherbrooke with a Mammouth supercomputer supported by le Réseau Québécois de Calculs de Haute Performances. The DFT²¹⁻²⁴ and TDDFT²⁵⁻²⁷ were calculated with the B3LYP²⁸⁻³⁰ method. 3-21G*³¹⁻³⁶ basis sets were used for C, H, N, F, and Cl, polarized basis sets for Pt,³⁷⁻³⁹ and VDZ (valence double ζ) with SBKJC effective core potentials⁴⁰⁻⁴² for platinum. The predicted phosphorescence wavelengths were obtained by energy differences between the triplet and singlet optimized states.⁴³ The calculated absorption spectra and related MO contributions were obtained from the TDDFT/singlets output file and Gaussum2.2.⁴⁴ The electrode potentials and orbital energies were obtained from the DFT calculations with a method like Namazian et al.'s.⁴⁵

Electrochemistry. Electrochemical experiments were carried out using a standard three-electrode configuration glass cell and a PAR

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273A potentiostat interfaced to a personal computer. The cyclic voltammetry (CV) was carried out at a working electrode Pt disk (5 mm diameter, Pine Chem) that had been polished to a mirror with 0.05 μ m Buehler paste and a Pt mesh as the counter-electrode. The potentials are reported vs the saturated calomel reference electrode (SCE). Electrochemical measurements were carried out at room temperature under a flow of argon. The supporting electrolyte was [NBu₄][PF₆] previously recrystallized from ethanol and vacuum-dried. The electrolytic solutions of 0.1 M [NBu₄][PF₆] were made in DMF. DMF (Fischer) was distilled under vacuum or used as received. Trifluoroacetic acid (TFA, Aldrich, 99%) was used as received. The concentration of the electroactive material was 4 mM.

RESULTS AND DISCUSSION

Synthesis. Compounds 1a-c were reduced using either hydroiodic acid or sodium borohydride to generate the corresponding diamino compounds 5a, 5b, and 5c (Scheme 1). These species provided single crystals of sufficient quality for X-ray diffraction analysis, providing useful information on their conformation and for structural comparisons with the corresponding diimines (see below). Model 5d was prepared in high yield from 3a using a mild reduction method (Zn + NH₄Cl), proving that this reduction method can indeed work on these imines. Consequently, the same method was used for the reduction of P3a-d in order to prepare the target mixed valence polymers P5a-d in good yields. The identity of the Pt-organometallic polymers was confirmed on the basis of IR, ¹H and ³¹P NMR, and their photophysical properties. Evidence for polymerization was obtained from gel permeation chromatography (GPC; Table 1). Noteworthy, the fully

Table 1. Molecular Weights and Dispersity Index for P5a-dObtained by GPC^a

	$M_{\rm n}$	$M_{ m w}$	DP	Đ
P5a	11 300	23 700	2.09	11
P5b	9200	15 700	1.71	9
P5c	6290	11 200	1.78	5
P5d	5140	7420	1.44	5
^{<i>a</i>} The average	molecular	weight in number	(M_n) , average	molecular

weight in weight (M_w) , dispersity index (D), and degree of polymerization (DP).

reduced versions of these polymers were never isolated despite the various synthesis methods used, leading to the conclusion that stability seems to be an issue. Only the mixed-valence form was obtained, suggesting that the presence of the oxidized fragment contributes to the stabilization of the polymers P5a-d.

The ³¹P NMR spectra of polymers **P5a**–**d** are characterized by a singlet in the vicinity of ~2.60 ppm (in CDCl₃) flanked by the expected ¹⁹⁵Pt satellites witnessing the ¹J_{Pt-P} coupling constant, while a single resonance is observed at ~2.85 ppm for **P3a**–**d** (Figure 1). The magnitudes of these coupling constants (~2385 Hz) are typical for a *trans*-geometry about the Pt atom.⁴⁷ The resonance peak expectedly shifts to higher field from 2.89 (**P3c**) to 2.86 (**P3b**), to 2.85 (**P3a**), and to 2.77 (**P3d**) for **P3a**–**d** (oxidized polymers) and from 2.66 (**P5c**) to 2.65 (**P5b**), to 2.59 (**P5a**), and to 2.56 (**P5d**) for **P5a**–**d** (mixed-valence form). Clearly, both the spacer (imine or amine) and the substituent (Br, H, NH₂) affect the electronic density at the Pt atom. The electron-withdrawing and -donating groups shift the ³¹P resonance to low and high field, respectively. Interestingly, only one resonance is observed for



Figure 1. ³¹P NMR spectra of **P3a-d** and **P5a-d** in $CDCl_3$ (the nature of the substituent is indicated for convenience). The 0 ppm is on the right-hand side on this figure. The small chemical shift changes due to substitution suggest that conjugation is modest.

the mixed-valence polymers P5a-d, meaning that the resulting signal is an average, perhaps resulting from chemical exchange (tautomers).¹⁰

X-ray Structure Determination. Electronic communication across a polymer via π -conjugation strongly depends upon the geometry and the π -orbital overlaps. Because of the recent findings that the NMe bridge secures electronic communication in P2,⁸ the X-ray structures of two new compounds containing the NH bridge between the anthracene and the phenyl groups have been analyzed, notably for **5a,b**, and compared with **5c** and the previously reported related diimine model compounds (Figure 2).^{9,10}

The dihedral angle ϕ made by the average plane of the 4phenylacetylene unit with the average plane made by the anthraquinone (1a-c, 1e, 2a) or anthracene (5a,b,d) units is reported as a function of the C=N and C-N bond length, respectively, in Figure 3 and Table 2. As the C-N bond is associated with a flexible single bond (1.39 < d(C-N) < 1.43)Å), the dihedral angle tends to be large $(70^{\circ} < \phi < 85^{\circ})$, reflecting the lack of efficient π -conjugation. Conversely, when the C=N bond is associated with a double bond (1.25 < d(C-N) < 1.31 Å), the dihedral angle tends to be somewhat smaller $(40^{\circ} < \phi < 65^{\circ})$, witnessing the presence of some π conjugation. While the diaminoanthracenes are planar, the AQ-containing species (i.e., anthraquinone diimine) are notoriously nonplanar, with dihedral angles ω being formed between the average planes of the benzene fragments of the AQ residue. These ω angles are $150.1(1)^{\circ}$ (1a), $156.4(1)^{\circ}$ (1b), $158.7(1)^{\circ}$ and $165.5(1)^{\circ}$ (1c; two crystallographycally independent molecules), $180.0(1)^{\circ}$ (1e), and $144.2(1)^{\circ}$ (2a)



Figure 2. Comparison of the ORTEP representations of the amine compounds 5a,b,d (top) and the quinone imine derivatives 1a-c,e and 2a (bottom). The thermal ellipsoids are represented at 30% probability. For 5b, there is a 50% occupation site for the Br atom attached to the anthracene aromatic group.



Figure 3. Graph reporting the dihedral angles (ϕ, θ) made by the phenyl-acetylene average plane with that for the anthraquinone diimine one (ϕ for **1a-c**, **1e**, **2a**) or 9,9'-anthracene (θ for **5a,b,c**) units, respectively, as a function of the average C==N or C-N bond lengths.

induced by steric interactions between the 4-phenylacetylene unit and the 1,1'-protons.

Compound 1e stands somewhat apart from the other diimine species in Figure 3 (i.e., longer C=N bond lengths and larger ϕ angle, ~63°, in its group) and with the rather planar anthraquinone structure ($\omega = 180^\circ$), suggesting the presence of an obvious 9,9'-diaminoanthracene character. Based on fluorescence and IR and ¹H NMR spectroscopic data for compounds 3d, 4d, and 5d, a tautomeric form was noted previously (Scheme 2). Now, these X-ray data for 1e adequately corroborate this finding but do not provide a way to quantify the relative ratio.¹⁰ On the basis of the position of 1e data points in the graph of Figure 3, the AQ form appears to be the dominant species (see structures on the left in Scheme 2).

Table 2. Metric Param	eters Describing	; the 9,9'-
Diaminoanthracene (A) and AQ Local	Structures ^a

	$d(C_6H_4-N)/Å$	(av) $d(\mathbf{A}-\mathbf{N})$	/Å ω/\deg	θ /deg (av)
$5a^b$	1.388	1.417	180	81.43
$5b^b$	1.382	1.427	180	78.78
$5d^c$	1.391	1.404	180	71.27
	$d(C_6H_4-N)/Å$ (av)	d(AQ=N)/Å (av)	$\omega/{ m deg}$	$\phi/{ m deg}$
1a ^d	1.424, 1.434 (1.429)	1.274, 1.306 (1.290)	150.12 4	5.47, 38.31 (41.89)
1b ^d	1.419, 1.477 (1.448)	1.237, 1.285 (1.261)	156.38 5	2.31, 48.68 (50.50)
1c ^d	1.420, 1.471 (1.446)	1.214, 1.269 (1.242)	158.66 5	7.96, 52.11 (55.04)
1c' ^d	1.391, 1.342 (1.367)	1.252, 1.272 (1.262)	165.53 6	7.94, 55.59 (61.77)
$1e^d$	1.393	1.304	180.00 6	3.27
2a ^c	1.415, 1.423 (1.419)	1.266, 1.266 (1.266)	144.18 5	4.35, 47.35 (50.85)

^{*a*}No uncertainties are provided for clarity and simplicity. These are less than 1% on each value. ^{*b*}This work. ^{*c*}From ref 10, but the stucture was not discussed in detail. ^{*d*}From ref 9, but the stucture was not discussed in detail.

Scheme 2. Possible Tautomeric Forms for the Amino-Containing Species 2d, 3d, and 4d (Top) and 2e, 3e, and 4e (Bottom; $R = SiMe_3$, H, and $Pt(PBu_3)_2Cl)^a$



^{*a*}On the left are the target compounds, and on the right are the tautomeric forms generated during the synthesis. Note that the dissymmetric tautomeric form is not represented in the series **2e**, **3e**, and **4e** for simplicity.

Thermal Stability. Two polymers were investigated by TGA (Figure 4) and exhibit no weight loss until reaching 350 $^{\circ}$ C for **P3e** and 400 $^{\circ}$ C for **P3b**, which are clearly reminiscent of that found for PANI.⁴⁶

The traces are characterized by a single plateau showing weight losses of respectively 32% and 37% (difference taken at 600 °C) for **P3b** and **P3e**. These weight losses may be attributable to the N,N'-diphenyl-**AQ** units, for which theoretical values of 36% and 41% are expected. Only a gradual weight loss is obversed in the TGA traces in the 600–950 °C range. As PANI does not exhibit a residual at this temperature,⁴⁶ these weight residuals may be attributed to the presence of Pt atoms in the chain.

Spectroscopic Signature of the 9,9'-Diaminoanthracene-Containing Species. During the course of this study, attempts to prepare the Pt-leucoemeraldine version of PANI and its Pt-containing model failed. For this reason, the diamino precursor 5d was used as a model instead. Compound 5d exhibits two absorption bands, at 427 and 290 nm (Figure 5, top). The interpretation of these two features in 5d has been



Figure 4. TGA traces (top) and their first derivatives (bottom) of P3b (left) and P3e (right). Scan rate = 10° /min.

addressed using DFT and TDDFT computations (Figure 5, bottom; also see detail in the SI).

Notoriously, the HOMO is composed of π -systems of all three fragments, the two terminal $C_6H_4C\equiv C$ (excluding the SiMe₃ groups) and the central anthracence residues (A), whereas the LUMO is composed only of the π -system of the central A unit. Any electronic transitions between these two frontier MOs leads to a CT band of the type $C_6H_4C\equiv C(\pi) \rightarrow$ $A(\pi^*)$. This observation also applies for the HOMO-2 \rightarrow LUMO and HOMO-1 \rightarrow LUMO transitions, as the HOMO-2 and HOMO-1 are also largely composed of the two terminal $C_6H_4C\equiv C$'s. The TDDFT computations (see data in the SI) place the two lowest energy transitions with non-nil intensity (oscillation strength, $f \neq 0$) at 480 (HOMO \rightarrow LUMO; 95%) and 375 nm (HOMO-2 \rightarrow LUMO; 94%). The 480 nm value falls where the 0-0 vibronic component is expected (near where the absorption and fluorescence traces cross). Interestingly, this CT process occurs with $\theta \approx 71^{\circ}$ (Figure 5).

The calculated 375 nm position also falls close to a feature observed at 350 nm. Thus, TDDFT computations indicate that the features located in the 350-550 nm window are also CT bands $(C_6H_4C \equiv C(\pi) \rightarrow A(\pi^*))$. The next computed intense electronic transition appears at 292 nm (f = 0.750) and is close to the more intense absorption band near 285 nm. The TDDFT calculations show that the major contributions are HOMO \rightarrow L+1 (57%) and HOMO \rightarrow L+3 (23%). These three MOs are composed of π -systems belonging to all three fragments of 5d (again excluding the SiMe₃ groups), and this band is more appropriately assigned to a $\pi\pi^*$ transition. The main conclusion of these calculations is that low-energy CT interactions occur between the unconjugated $C_6H_4C\equiv C$ units and the central A (anthraquinone) residue despite the unfavorable dihedral angles discussed above. This observation corroborates well with the conclusion made for polymer P2, where an intense red-shifted CT band was noted as well.⁸

The effect of linking [Pt] on the 1,4-diaminoanthracene unit (i.e., C_6H_4NH -A- NHC_6H_4 ; A = anthracene) was also examined from a theoretical standpoint (DFT/TDDFT) for a model denoted as (HC \equiv CC₆H₄-**NH**-A-**NH**-C₆H₄C \equiv C)₂-[Pt]- (Figure 6 and detail in the SI). The LUMO and LUMO+1 are composed of atomic contributions placed on the π -systems of the two 1,4-diaminobenzene units, consistent with that calculated for **5d**. The HOMO to the HOMO–4 exhibit atomic contributions of π -systems comprising all fragments of the model (excluding the H atoms), again consistent with that computed for **5d** (Figure 5), but also include the presence of the conjugated $Pt(d_{yz})$ atomic orbital. This contribution contrasts with the quasi absence of atomic contributions from the SiMe₃ groups, and therefore the electronic properties are bound to be different from compound **5d**.

Indeed, TDDFT computations (see the SI) indicate that the four lowest energy transitions (between 455 and 535 nm) are all CT processes of the type $C_6H_4C\equiv C-Pt(\pi) \rightarrow A(\pi^*)$. The computed predicted red-shift of the lowest energy CT transition going from compound 5d to (HC=CC₆H₄-NH-A-NH-C₆H₄C \equiv C)₂-[Pt]- (or its Pt-containing polymer) is 55 nm (i.e., 2110 cm⁻¹). This value is consistent with that experimentally observed, for example, the Q-containing polymer **P1a** (λ_{max} = 502 nm) with respect to its corresponding Q spacer Me₃SiC \equiv CC₆H₄-N=C₆Me₄=N-C₆H₄C \equiv CSiMe₃ $(\lambda_{max} = 446 \text{ nm})$ in 2MeTHF at 298 K (i.e., 502–446 = 56 nm; i.e., 2500 cm⁻¹).^{6b} Large red-shifts were also observed for polymers P1b-e vs their corresponding spacers Me₃SiC≡ CC_6H_4 -N= C_6X_4 =N- C_6H_4C = $CSiMe_3$ (X = OMe, H, F, Cl; $3280 \pm 450 \text{ cm}^{-1}$).⁶ The conclusion is that the Pt version of leucoemeraldine is still currently synthetically elusive, but both theory and experiments expectedly predict a red-shift of the CT band upon addition of the [Pt] residue.

Spectroscopic Signature of the *N*,*N*'-Anthraquinone Diimine-Containing Species. The 298 and 77 K absorption spectra for selected polymers are shown in Figures 7 and 8, and the data for the model compounds and polymers are summarized in Table 3. The key feature is the presence of the low-energy broad CT bands of the type $C_6H_4C\equiv C-Pt(\pi)$ $\rightarrow AQ(\pi^*)$ in the 350–600 nm region as previously assigned on the basis of the striking resemblance with the spectra of the corresponding Q-containing polymer^{6,7} and previous DFT/ TDDFT computations for HC \equiv C-AQ-[Pt]-AQ-C \equiv CH ([Pt] = $C_6H_4C\equiv$ CPt(PMe₃)₂C \equiv CC₆H₄; AQ = 2,6-diami**Organometallics**



Figure 5. Top: Absorption (black; $\varepsilon = 13500$ (427 nm) and 83400 M^{-1} cm⁻¹ (290 nm)), fluorescence (red; $\lambda_{Fluo} = 520$ nm; $\tau_F = 4.5 \pm 0.1$ ns; $\Phi_F = 0.16 \pm 0.02$), and excitation (blue) spectra of **5d** in 2MeTHF at 298 K. The green bars are the computed electronic transitions of **5d** in the solvent field of THF (TDDFT; B3LYP). Bottom: Representations of the frontier MOs of **5d**.

noanthraquinone diimine).⁹ However, apparent anomalies in the position and relative intensity of the CT band are noted.

Prior to commenting on the position of the CT bands, their relative intensities are addressed. The absorption CT bands of mixed-valence polymers **P5a-d** expectedly become weaker than that of the fully oxidized versions **P3a-d** (Figure 8; the ε data are in Table 3). In order to get an approximate ratio of the amount of imine and amine within these polymers, the absorptivity at 550 nm was measured knowing that the amine-containing model does not absorb at all in this region (see Figure 5). Qualitatively, the results (from $A_{P5a-d} = \varepsilon_{(550 \text{ nm}, P3a-d)} \times l \times c_{(unit in P5a-d)})$ indicate a imine/amine ratio



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Figure 6. Top: Representations of the frontier MOs of the (HC \equiv CC₆H₄-**NH-A-NH-C**₆H₄C \equiv C)₂-[**Pt**]- model (see structure in the frame below). Because the SiMe₃ groups have practically no atomic contribution in compound **5d**, these residues were not used. Bottom: Computed positions of the electronic transitions of (HC \equiv C-**NH-A-NH**)₂-[**Pt**]- (bars). Their values and *f* data are available in the SI. The blue line represents the calculated spectrum (without the vibronic components), assigning a thickness of 1000 cm⁻¹ for each transition.

of ~1 in the polymers P5a-d. As for the position, in the polymers P3a-e, the Br and NH₂ substituents on AQ are respectively electron withdrawing and donating. Consequently, the $C_6H_4C\equiv C-Pt(\pi) \rightarrow AQ(\pi^*)$ CT band should red- and blue-shift, respectively, based on the well-established behavior reported for the quinone diimine-containing polymers P1a-e.⁶ At 298 K, this behavior is indeed noted, but at 77 K, where the spectra are more vibronically defined for the high-energy features and somewhat broader for the low-energy CT band, the amino-AQ-containing polymers P3d,e exhibit a slight red-shift of the CT band with respect to the nonsubstituted polymer P3a (Figure 7; bottom right). This is a little



Figure 7. Absorption spectra of **P3a,c**-**e** in 2MeTHF at 298 (left) and 77 K (right).



Figure 8. Comparison of the absorption spectra of P5a and P3a (left) and P5d and P3d (right) in THF at 298 K.

	298 K	77 K
	$\lambda_{\max} (nm) (\epsilon (M^{-1} cm^{-1}))$	λ_{\max} (nm)
2a	250 (49 600), 292 (61 000), 417 (11 000)	254, 272, 298, 426
2b	258 (139 000), 292 (122 000), 425 (23 300)	
2c	264 (102 000), 292 (63 700), 450 (7940)	270, 296, 450
2d	250 (78 800), 290 (92 800), 420 (20 100)	275sh, 298, 432
2e	290 (154 000), 330sh (58 200), 375sh (54 300), 430sh (38 100)	260, 296, 350, 460sh
4a	248 (67 200), 293 (50 600), 320 (44 700), 467 (14 300)	284sh, 310sh, 326, 474
4b	250 (79 200), 290sh (5530), 424 (10 600)	260, 294, 326, 430
4c	262 (56 100), 290 (36 300), 322 (24 100), 513 (6000)	266, 300, 328, 515
4d	243 (84 900), 295 (81 700), 326sh (50 900), 440 (20 300)	304, 326, 455
4e	242 (39 100), 290 (40 700), 455 (12 700)	285sh, 308, 326, 472
P3a	330 (22 500), 460 (7500)	300, 334, 460
P3b	330 (23 700), 451 (4500)	300, 340, 452
P3c	330 (28 900), 471 (7750), 500 (6800)	310, 340, 500
P3d	330 (23 100), 435 (12 100)	300, 330, 445
P3e	250 (8500), 290 (12 800), 335 (9000), 430 (2300)	300, 340, 385, 474
P5a	288 (26 200), 344 (11 000), 463 (3700)	300, 342, 462
P5b	291 (29 600), 346 (15 200), 469 (4400)	300, 358, 470
P5c	300 (26 500), 345 (18 300), 488 (4800)	338, 364, 496
P5d	300 (25 600), 355 (13 800), 455 (5700)	300, 346, 456

Table 3. Absorption Data in 2MeTHF

unexpected, but the large bandwidth (>100 nm) may blur the real position of the band. Nonetheless, no obvious blue-shift is noted. Because of this unexpected result, the UV-vis spectra of the model compounds 2a-e and 4a-e were also examined, and this observation also qualitatively applies. Compound 4b appears to be an exception, as the CT band shifts to the blue instead of to the red. No reason can be provided at this point for this specific case. In order to provide a tentative explanation for the general substituent effect on the position of the CT band (mainly the HOMO-LUMO energy gap), DFT computations were performed (Figure 9). First, calculations



Figure 9. Comparison of the energy levels of the frontier MOs for the model compounds ($HC\equiv CC_6H_4$ -AQ(X,X')- $C_6H_4C\equiv C)_2$ -[Pt]- and ($HC\equiv CC_6H_4$ NH-A-NHC₆ $H_4C\equiv C)_2$ -[Pt]-. No solvent field was applied in these calculations to preclude any solvent–molecule interactions.

on the model compounds (HC \equiv CC₆H₄-AQ(X,X')-C₆H₄C \equiv $C_{2}-[Pt] - ([Pt] = C_{6}H_{4}C \equiv CPt(PMe_{3})_{2}C \equiv CC_{6}H_{4};$ AQ(X,X') = X,X'-substituted AQ) were performed. The MO diagrams are provided in the SI and are reminiscent of those presented in Figure 6 (top). The key feature is the steady increase in HOMO-LUMO gap according to the substitution $X_{,}X' = Br_{,}Br(2.48); H_{,}Br(2.53); H_{,}H(2.59); H_{,}NH_{2}(2.61);$ and NH₂,NH₂ (2.78 eV), a trend that is expected for the inductive effect. Indeed, the electron-withdrawing Br stabilizes the MOs (by reducing the electron-electron repulsions on the π -system), whereas the opposite occurs with the electrondonating NH₂ group. However, the LUMO is almost entirely localized on the AQ units, and so the inductive effect is far more pronounced relative to that for the more spread filled MOs (i.e., on both the [Pt] and AQ residues). This situation results in a smaller and larger HOMO-LUMO gap and consequently a red- or a blue-shift of the CT band upon the use of an electron-withdrawing or -donating group.

During the course of these calculations, the fully reduced version model $HC \equiv CC_6H_4$ -A-[Pt]-A- $C_6H_4C \equiv CH$ (A = anthracene) was also compared. The similarity in MO shapes (SI) and energies with the diamino derivatives is striking (Figure 9; HOMO-LUMO gap = 2.86 eV). We propose that the unexpected red-shift of the CT band observed for P3a vs P3c upon the replacement of H by NH₂ (instead of a blue-shift) can be caused by two possible effects. The first one is the common specific interactions with the solvent. In the case of 2MeTHF, a H-bond, N-H…O, can occur and a global notable red-shift of the CT band is then expected, which amplifies upon

cooling to 77 K (as observed). Indeed, generally the CT nature of this excited state involves a stronger stabilization in polar media, an effect that is amplified upon stronger H-bonding interactions. The second effect that could induce a global redshift of the CT band is the presence of tautomers (Scheme 2). This proposal is made since the computed position of the lowest energy transition for the C=N-H-containing tautomer (see drawing of the model in Figure 10) is red-shifted (658.6



Figure 10. Computed positions of the electronic transitions of the tautomer containing the C=N-H units. Their values and *f* data are available in the SI. The blue line represents the calculated spectrum (without the vibronic component), assigning a thickness of 1000 cm⁻¹ for each transition. The blue and red colors are to differentiate the two tautomeric forms.

nm, f = 0.431) comparatively to the $-NH_2$ derivative (575.7) nm, f = 0.222, SI). This computation provides only a qualitative suggestion since the relative amount of C=N-H-containing tautomeric units (i.e., its relative contribution) in the chain is unknown. However, its occurrence is presumably much less than that for the $-NH_2$ one based on the X-ray structure of compound **1e** (see position **1e** relative to the other in Figure 3; i.e., the C=N distance appears as an elongated double bond). However, it is interesting to note that the computed position of the low-energy CT band is >650 nm, a position that is in the correct vicinity of the experimentally observed CT band in PANI in its (mixed-valence) emeraldine form, spreading from 550 to 750 nm.⁴⁶ Recent TDDFT calculations on PANI also placed the 0-0 peak of emeraldine at 600 nm.⁴⁷ One may conclude that the coloration of unprotonated emeraldine is due to the combination of imine and amine functions in the polymer backbone. Noteworthy, the protonated version of PANI exhibits a red-shifted maximum to ~830 nm, spreading to 1000-1100 nm.48

Electrochemical Measurements. The CVs for 2a-c exhibit reduction processes in the -2.0 to +0.5 V vs SCE range (Figure 11; no signal is detected above 0 V until the oxidation limit of the solvent). These traces are notably chemically irreversible, and the peak reduction potentials (-1.181 (2a), -1.000 V (2b), and -0.954 V (2c)) follow the trend of the LUMO energy (Figure 9, i.e., E(LUMO) for dibromo- < monobromo- < unsubstituted AQ), thus reflecting the Br inductive effect (i.e., electron poorer AO means easier to reduce). For the amino series, the waves are also irreversible. Again, one would expect that the more electron donating group would induce more negative potentials for the reduction processes for the NH₂-substituted species, but the reverse is observed (-1.181 (2a), -1.138 (2d), and -0.934 V (2e) vs SCE). This trend corroborates the unexpected red-shift (instead of blue-shift) of the CT band for these same NH₂containing species (2a, 417; 2d, 420; 2e, 430 nm; data from Table 3).

The Pt-containing model complexes 4a-c and polymers P3a-c exhibit far more complex CV traces than that recorded for 2a-c (Figure 11, left), where several wave splittings are observed. The polymers P3a-c exhibit simpler patterns to interpret where essentially chemically reversible (but electrochemically irreversible) processes are noted. The lower reduction potentials are -0.969 V (P3a), -0.837 V (P3b), and -0.696 V (P3c) and follow the expected trend for the Br substitution. Although the splitting of the reduction waves for 2d (Figure 11) and P3b can be associated with a reduction of symmetry in AQ, the presence of four distinct waves for P3c remains obscure.

The CV traces for the Pt-containing model compounds 4a-c are notoriously complex (Figure 12, left), and attempts to reliably interpret the data would be futile. Upon addition of acid (0.7 M trifluoroacetic acid), the reduction waves expectedly shift to more positive potentials (i.e., -0.2 to 1.0 V vs SCE), consistent with the predicted protonation of the imine functions. However, the traces drastically change shape and exhibit multiple waves, which are either chemically (mostly for the polymers P3a-c) or electrochemically irreversible (mostly for 4a-c). The presence of chemically irreversible waves indicates instability at the time scale of the CV measurements. The signal in the vicinity of +1.1 V vs SCE is associated with the oxidation of the [Pt] unit.^{6a,b} The main conclusion is that the target polymers are electroactive in the -0.1 to -1.5 V window and -0.2 to +1.0 V vs SCE in the absence and presence of 0.7 M acid, respectively, which makes the materials potentially useful for applications listed in the introduction.



Figure 11. CV of 2a-e in DMF (4 mM) with 0.1 M of TBAPF₆. Scan rate = 100 mV/s.

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Figure 12. Left: CV of 4a-c and P3a-c in DMF (4 mM) with 0.1 M TBAPF₆. Scan rate = 100 mV/s. Right: CV of 4a-c and P3a-c in DMF (4 mM) with 0.1 M TBAPF₆. Scan rate = 100 mV/s with 0.7 M trifluoroacetic acid.

				,								
Table -	4. Emission	Lifetime	Data (2MeTHF:	AO =	Anthraa	uinone	diimine:	A = 1	Diaminoai	nthracene)"
I uvic	. Liniooion	Directime	Dutu	(21,10 I I I I)		1 minung	amone	annie,		<i>c</i> iumitoui	i u come	/

	λ_{\max}	$ au_{ m F}~({ m ns})$ and $ au_{ m P}~(\mu{ m s})$		$\lambda_{ m max}$	$ au_{ m F}$ (ns) and $ au_{ m P}$ (μ s)
5d (298 K)	520	$4.52 \pm 0.10 \text{ ns} (A)$		535	<0.1 ns (A ?)
5d (77 K)	510	$6.09 \pm 0.10 \text{ ns} (\mathbf{A})$	P3e (77 K)	410	$0.28 \pm 0.01 \text{ ns} (AQ)$
2a (77 K)	340	$0.25 \pm 0.10 \text{ ns} (AQ)$		weak	
	440	$2460 \pm 90 \ \mu s \ (AQ)$		455	$60.5 \pm 0.4 \ \mu s (AQ)$
2b (77 K)	450	0.13 ± 0.10 ns (AQ)	P5a (298 K)	527	<0.1 ns (<2%) (AQ?), 1.1 ± 0.2 ns (15%), 3.7 ± 0.2 ns (83%) (A)
	487	$24.9 \pm 2.8 \ \mu s \ (95\%) \ (AQ)$	P5a (77 K)	509	1.67 ± 0.26 ns (1%), 5.1 ± 0.1 ns (33%), 8.9 ± 0.1
2c (77 K)	490	1170 ± 175 (60%), $5042 \pm 236 \ \mu s$ (40%) (AQ)	10 u (// 10)	007	ns (66%) (A)
2d (77 K)	340	$0.12 \pm 0.10 \text{ ns} (AQ)$	P5b	542	0.51 ± 0.16 ns (4%), 2.4 ± 0.1 ns (43%), 5.2 ± 0.1
	435 ^b	88.1 ± 6.8 and $50.0 \pm 5.0 \ \mu s$ (AQ)	(298 K)		ns (53%) (A)
- ()	535	- ^c	P5b (77 K)	550	1.02 ± 0.21 ns (2%), 3.6 ± 0.1 ns (28%), 7.2 ± 0.2 ns (71%) (A)
2e (77 K)	390	<0.1 ns (AQ)	P5c	559	0.59 ± 0.13 ns (9%), 2.2 ± 0.1 ns (29%), 4.7 ± 0.1
. ()	470	$38.1 \pm 1.8 \ \mu s (AQ)$	(298 K)	007	ns (62%) (A)
4a (77 K)	380 weak	<0.1 ns (AQ)	P5c (77 K)	582	0.84 ± 0.16 ns (3%), 3.1 ± 0.1 ns (28%), 7.4 ± 0.1 ns (69%) (A)
- ()	455	$64.8 \pm 0.4 \ \mu s \ (AQ)$	P 5d	544	0.44 ± 0.16 ns (20%), 2.2 ± 0.1 ns (18%), 6.9 ± 0.1
4b (77 K)	445	$43.1 \pm 1.4 \ \mu s \ (AQ)$	(298 K)		ns (62%) (A)
· (··)	480	$34.9 \pm 0.7 \ \mu s (AQ)$	P 5d	533	$0.97 \pm 0.09 \text{ ns} (2\%), 5.9 \pm 0.1 \text{ ns} (17\%), 12.0 \pm 0.1 \text{ ns} (1$
4c (77 K)	415 weak	$0.69 \pm 0.10 \text{ ns} (AQ)$	(// K)	c	$h = \frac{h}{h}$
	490	$79.7 \pm 2.9 \ \mu s \ (AQ)$	$\lambda_{\rm exc} = 365$	nm for	all cases. Occasionally, the phosphorescence
4d (77 K)	380	<0.1 ns (AO)	biexponentia	all but for	r other occasions they were single exponentia
	455 ^b	$71.1 \pm 0.3 \ \mu s$ (AQ)	with no spe	ecific tren	nd. Moreover, the relative intensities of these
	540	_d , (C	components	are λ_{exc}	dependent, consistent with the presence of two
4e (77 K)	395	<0.1 ns (AQ)	distinct spec	ies. These	e components are believed to be associated with
. ,	weak		various conf	ormations	s of the anthraquinone diimine units, which car
	455	$64.8 \pm 0.7 \ \mu s \ (AQ)$	form a butte	erfly or a	U-shaped structure. Also, cis-trans isomerism is
P3a (77 K)	380	$0.34 \pm 0.10 \text{ ns} (AQ)$	possible for	the anth	raquinone diimine structure depending on the
	460 ^b	$33.4 \pm 7.7 (55\%), 76.2 \pm 2.4 (45\%) \ \mu s (AQ)$	relative orie	entation of	of the C_6H_4 groups to each other, as well
P3b (77 K)	410 weak	$0.16 \pm 0.10 \text{ ns} (AQ)$	not the purp	on ref 8.	is work. Their lifetimes are used to confirm the
	444	$32.4 \pm 0.3 \ \mu s \ (AQ)$	presence of	the typic	cal $T_2 \rightarrow S_0$ phosphorescence arising from the
P3c (77 K)	460	$75.6 \pm 4.6 \ \mu s \ (AQ)$	quinone diir	nine chroi	mophore (see ref 5 in the text). Not measured
	490	$46.3 \pm 0.1 \ \mu s \ (AQ)$	Heavily mi	xed with t	ine phosphorescence and could not be extracted
P 3d (77 K)	410 weak	0.61 ± 0.10 ns (AQ)	of some of t	the compo	ore description of the multiexponential behavior ounds and polymers.
	445 ^b	60.3 \pm 0.7 and 33.2 \pm 0.4 μs (AQ)			

The Pt- and NH₂-containing model compound 4e and polymers P3d,e exhibit complex and ill-defined CV traces (i.e., all chemically irreversible; the traces are placed in the SI). These results are not surprising for compound 4e since the traces for 4a-c exhibit irreversible waves as well, likely reflecting the presence of the conjugated Pt(PBu₃)₂Cl groups. However, the comparison of the CV traces of P3a-c with those for P3d,e indicates that the loss of chemical reversibility must be associated with the presence of NH₂ groups. Because of this irreversibility, these polymers were not studied further as well as P5a-d.

Fluorescence Spectra and Photophysics. The photophysic details are placed in Table 4. The A-containing species Sd (A = 9,10-diaminoanthracene) is strongly fluorescent at 298 K (i.e., $\Phi_F = 0.16 \pm 0.02$, $\tau_F = 4.52 \pm 0.10$ ns, Figure 5, top), while all AQ-containing species are not at all. This behavior as well as the position and band shape of this characteristic fluorescence turns out to be particularly useful for the detection of A-containing residues in the materials, notably for polymers P5a-d. At 77 K, the AQ species become moderately emissive, and the presence of a fluorescence in the 350–400 nm region and a structured emission in the 450–550 nm window is reminiscent of that observed for PANI (emeraldine form) as a film on Pt electrodes^{49a,b} and in solution.^{49c,d} A representative example is provided in Figure 13. The comparison of the



Figure 13. Absorption (black), fluorescence (red), and excitation (blue) spectra of 5d, 2a, 4a, and P3a in 2MeTHF at 77 K.

fluorescence band of **5d** ($\lambda_{Fluo} = 520 \text{ nm}$; $\tau_F = 6.09 \pm 0.09 \text{ ns}$) with that of **2a** is quite revealing. For the latter model, a fluorescence and a phosphorescence band are depicted at 350 ($\tau_F = 0.25 \pm 0.02 \text{ ns}$) and 440 nm (0–0 peak, $\tau_P = 2460 \pm 90 \mu s$), respectively, and are notoriously placed above the CT origin (i.e., 0–0 peak) expected in the vicinity of 500 nm (unresolved). These two bands are unambiguously assigned to $C_6H_4C \equiv C \pi \pi^*$ excited-state emissions. In this case, these emissions are clearly violating Kasha's rule.

Compound 4a and polymer P3a also exhibit the same spectral traits as for 2a (again at 77 K). The absence or decrease in relative intensity of the fluorescence can be ascribed to the presence of [Pt]-containing groups (heavy atom effect). All these spectral signatures are identical to those previously unraveled for the Q-containing polymers P1a-e, suggesting that the skeleton of the acceptor chromophore is not responsible for the absence of fluorescence arising from the CT singlet state, which is most likely expected (and coincidently) in the 550 nm range for this series. In search for this CT fluorescence, the series 2d,e, 4d,e, and P3d,e was examined (Figure 14).



Figure 14. Absorption (black), fluorescence (red, orange), and excitation (blue, green) spectra of compounds 2d,e and 4d,e and polymers P3d,e in 2MeTHF at 77 K.

For compounds 2d and 4d, such an emission was detected, as well as those for the upper energy $C_6H_4C\equiv C \pi\pi^*$ fluorescence and phosphorescence, upon changing the excitation wavelength (λ_{ex}). However, these two sets of emissions cannot be assigned to the same chromophore, as the excitation spectra are different. There are three key elements. First, the spectral signatures of the emission spectra for 4a,d,e and P3a,d,e are quiet similar to that reported for Pla-e and P2⁶⁻⁸ as well as their related core complex $C_6H_5C\equiv C-Pt(PBu_3)_2-C\equiv CC_6H_5$.⁵⁰ In the latter study, a full vibronic analysis was performed along with DFT computations by Brozik and collaborators in which the authors conclude that the emissive state is a mixture of $\pi\pi^*$ and MLCT. Consequently, the nature of the emissive state for these species is bound to be the same. The conclusion is fully consistent with the DFT and TDDFT computations presented in this work. Second, there is a presence of a weak feature centered at \sim 460 nm in the excitation spectra (blue trace; Figure 14), which is not matching the absorption CT band and is reminiscent of that observed for the AQ compound 5d (Figure 13). Third, this 530 nm fluorescence band (orange line) resembles in shape that of 5d, which is somewhat red-shifted comparatively to 520 nm. Again as previously reported, the ¹H NMR and IR data reveal the presence of more than one type of NH function (i.e., amine and imine), evidencing the presence of tautomers (Scheme 2). Another piece of evidence for the tautomers is the spectra of 2b and 4b measured at 298 K (SI). Generally, the Q species are strictly nonemissive at room temperature. In these two cases, a weak ($\Phi_{\rm F} = 0.0010$) and a moderate ($\Phi_{\rm F} = 0.0038$) unstructured fluorescence at 550 (2d) and 567 nm (4d) are respectively depicted, and their excitation spectra exhibit the same features as stated above (i.e., the excitation band does not match the CT absorption). Their $\tau_{\rm F}$ values are essentially the same as for 5d ($\tau_{\rm F}$ = 4.5 ± 0.1 vs $\tau_{\rm F}$ = 4.6 ± 0.1 (2d) and 4.5 ± 0.1 ns (4d) when considering the uncertainties. However, the spectra of P3d at 77 K do not exhibit this fluorescence at 567 nm (Figure 14, bottom) as verified by the measurements of a possible decay on the nanosecond time scale in this spectral range. For 2e, 4e, and P3e, the presence of two amino groups

in the AQ structure suggests a larger occurrence of this tautomer emission in comparison with 2d, 4d, and P3d, respectively, expected at 550, 567, and 567 nm, with lifetimes on the nanosecond time scale. However, there is no evidence for such a tautomer fluorescence at 77 K for 2e, 4e, and P3e (Figure 14, right), and these materials are also found to be nonemissive at 298 K, contrasting with the series 2d, 4d, and P3d. Again, the crystal structure of the planar AQ-containing compound 1e along with the apparently elongated C=N bond is unambiguous about the presence of tautomers (Figure 2). One can only come to the conclusion that these 2e, 4e, and P3e species exhibit large nonradiative rate constants, k_{nrr} , relative to the radiative one (k_r) , particularly for the polymers.

The Br-containing series 2b, 4b, and P3b (mono-) and 2c, 4c, and P3c (dibromo-) are unsurprisingly nonemissive at 298 K. At 77 K, the emission spectra exhibit notable vibronic features where the apparent 0–0 peaks (~450 nm) are again placed at higher energies than the unresolved expected origin for the CT absorption (Figure 15). The emission lifetimes of



Figure 15. Absorption (black), fluorescence (red), and excitation (blue) spectra of compounds 2b, 4b, 2c, and 4c and polymers P3b and P3c in 2MeTHF at 77 K.

these features are all on the microsecond time scale, again indicating that these emissions are phosphorescence arising from an upper excited state. The spectral signature of the emission spectra of **4b,c** and **P3b,c** differs from those for **4a,d,e** and **P3a,d,e**, but the spacing between the main vibronic peaks averages $1650 \pm 150 \text{ cm}^{-1}$. This value compares favorably to that reported for $C_6H_5C \equiv C-Pt(PBu_3)_2-C \equiv CC_6H_5$ by Brozik and collaborators (1652 cm^{-1}).⁵⁰ These results corroborate the computational findings that the nature of these emissive excited states is again the same for **4b,c** and **P3b,c** as well as for **4a,d,e** and **P3a,d,e** (the DFT data are placed in the SI, Figures S1–S4).

For the mixed-valence polymers **P5a-d**, the spectroscopic and photophysical features are significanly different from the corresponding fully oxidized versions **P3a-d** (Figures 16 and 17). The polymers are emissive at both temperatures 298 and 77 K. The emission signature is unquestionably reminiscent of that for the **A**-containing residue (Figures 5 and 13) for model **5d**, but some clear discrepancies are noticed between the excitation and absorption spectra. The excitation spectra bear a strong similarity to the absorption ones of the **A**-fragment, again by comparison with the spectra of model **5d**. This



Figure 16. Absorption (black), fluorescence (red), and excitation (blue) spectra of P5a,b in 2MeTHF.



Figure 17. Absorption (black), fluorescence (red), and excitation (blue) spectra of P5c,d in 2MeTHF.

expected result stems from the larger fluorescence intensity of the A-containing chromophore relative to the AQ ones, as stated above (for 5d, $\Phi_F = 0.16 \pm 0.02$, whereas the imine-containing species are not or very weakly fluorescent at 298 K). Moreover, there is no evidence for phosphorescence (i.e., no lifetime on the microsecond time scale) at 77 K generally associated with the imine fragment for P5a–d (Table 4).

The absence of emission lifetimes on the microsecond time scale at 77 K, thus excluding evidence for phosphorescence arising from the **AQ** residues (i.e., $T_2 \rightarrow S_0$) even with the use of time-resolved spectroscopy, is interesting. This apparent quenching is associated with intrachain energy transfer $T_2(AQ) \rightarrow T_n/S_n(A)$. Energy transfer along the backbone of a [**Pt**]-containing polymer is well known.⁵¹

CONCLUSION

The fully oxidized Pt-containing version of PANI, $(-AQ-[Pt])_n$, has been investigated using various optical and physical techniques, notably examining the substitution effect with electron donors (NH_2) and acceptors (Br) on the AQ residues. The interpretation of the data was aided by the use of model compounds and DFT and TDDFT calculations. The inductive effect of these substituents was indeed corroborated by both electrochemical and UV–vis optical measurements, where the position of the reduction peaks followed that of the absorption. Although not formally investigated or commented on, conjugation is possible but appears somewhat modest in these polymers, as illustrated in Figure 1 (the ³¹P NMR chemical shift changes modestly with the substituent). The

characteristic spectral signature is directed by a CT interaction between the electron rich -[Pt]- unit and AQ in absorption spectra and the $T_2 \rightarrow S_0$ phosphorescence (located in the [Pt] fragment). This CT behavior was also noted for the Acontaining model 5d, a compound that exhibits only amino groups and is formally unconjugated. Attempts to prepare the corresponding fully reduced Pt-containing version of PANI, (-A-[Pt]-)_n, stubbornly failed, where at best the corresponding mixed valence versions of these polymers were isolated ((-A-[Pt]-)_x(-AQ-[Pt]-)_y)_n with an approximate A/AQ ratio of ~1 in all cases. The emission properties of the latter are dominated by the fluorescence of the diamino-containing units, A^{*}, where complete quenching of the AQ emission is observed, most likely via energy transfers (T₂(AQ) \rightarrow T_w/S_w(A)).

Another salient point is the presence of a tautomeric form, previously demonstrated by spectroscopic techniques but corroborated by X-ray crystallography in this work. The use of NH₂ substituents on AQ opens the door to the design of what would be a fully oxidized version of the $([Pt]-AQ)_n$ polymers, but instead the presence of tautomer units within this same chain places amino groups in the polymer backbone at the same time, thus generating a mixed-valence form of this material. This approach is unique and clearly convenient.

All in all, the chemistry of PANI is rich (see Introduction), and the thermally stable Pt–organometallic versions (fully oxidized and mixed valence) also exhibit rich (and complex) electrochemical (in nonacid and acid media) and photophysical properties. The main difference so far between the [Pt]-containing polymers reported herein and PANI is the rather low fluorescence intensity and, to the best of our knowledge, the absence of phosphorescence for the latter material in its various forms as reported in the literature, a behavior recently explained by the presence of C–C single bonds in the polymer structure, notably from emeraldine.⁵² The design of devices similar to those using PANI is yet to be reported of the organometallic version of this interesting polymer, and on the basis of the results assembled here, one can easily anticipate that the same devices can be fabricated and investigated.

Deposited Structures. Compound 5a, CCDC 1008864; compound 5b, CCDC 1008863.

ASSOCIATED CONTENT

S Supporting Information

Images of the representations of the frontier MOs, crystallographic tables for **5a** and **5b**. Representations of the frontier MOs of the (HC \equiv CC₆H₄-NHANH-C₆H₄C \equiv C)₂-[Pt]-, (HC \equiv CC₆H₄-AQ-C₆H₄C \equiv C)₂-[Pt]-, (HC \equiv CC₆H₄-AQBr-C₆H₄C \equiv C)₂-[Pt]-, (HC \equiv CC₆H₄-AQBr₂-C₆H₄C \equiv C)₂-[Pt]-, (HC \equiv CC₆H₄-AQ(NH₂))-C₆H₄C \equiv C)₂-[Pt]-, and (HC \equiv CC₆H₄-AQ(NH₂))-C₆H₄C \equiv C)₂-[Pt]-, and (HC \equiv CC₆H₄-AQ(NH₂))-C₆H₄C \equiv C)₂-[Pt]- models, comparison of the CV traces of **4a**,e and P**3a**,d,e in DMF with 0.1 M TBAPF₆, comparaison of the absorption, fluorescence, and excitation spectra of **5c**, **2d**, and **4d** in 2MeTHF at 298 K. Computed positions of the electronic transitions, the oscillator strength (*f*), and the major contributions of the tautomer model compound, all crystal and structure data for **5a** and **5b**. ¹H and ¹³C NMR spectra of **5a–e**, P**3a–d**, and P**5a–d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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