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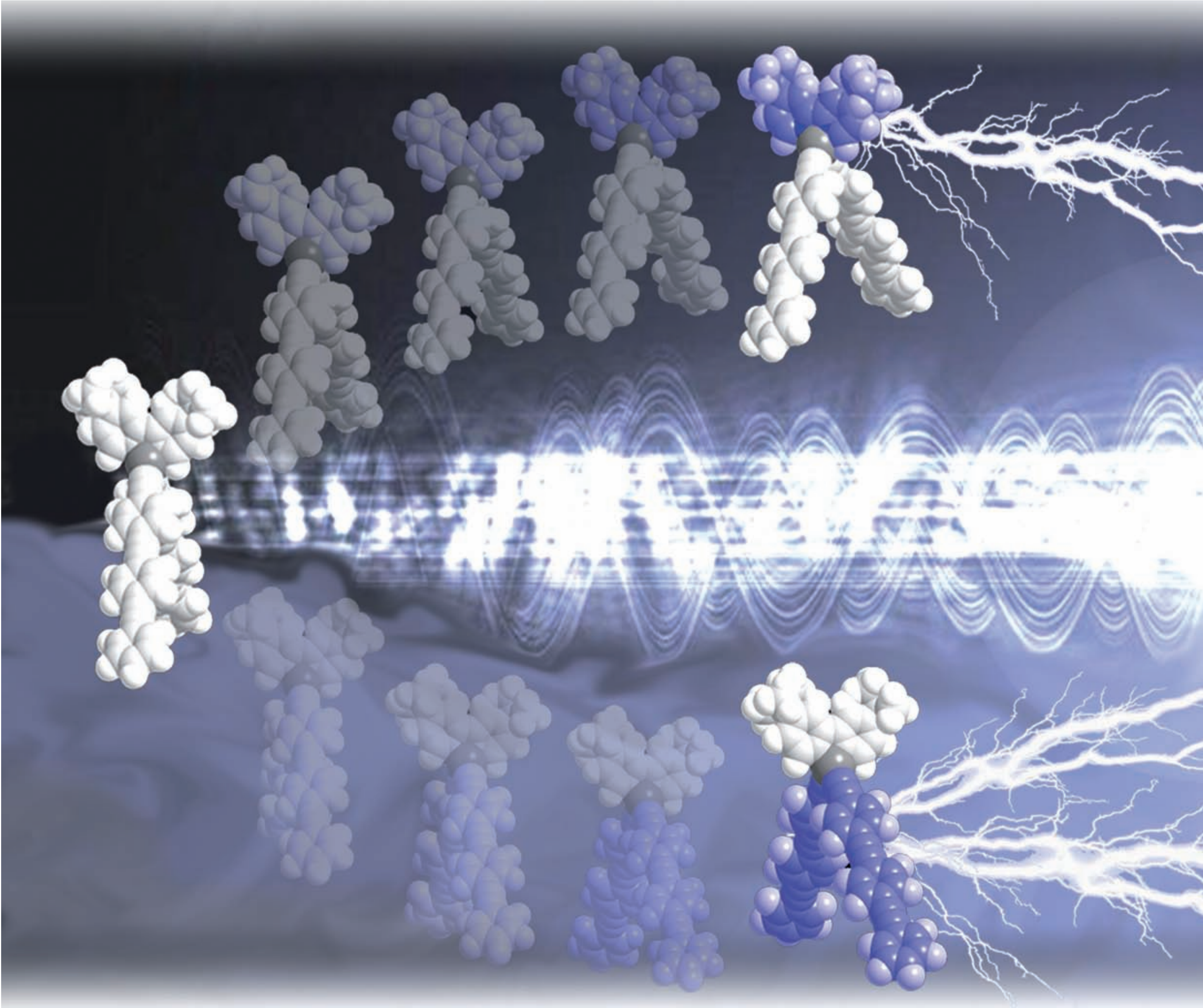

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Solvent-induced configuration mixing and triplet excited state inversion exemplified in a Pt(II) complex†

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The present study provides clear-cut experimental evidence for solvent-induced configuration mixing and complete triplet state inversion at room temperature in a Pt(II) charge transfer complex bearing a combination of energetically proximate charge transfer and intraligand triplet excited states.

The quest for molecular structures possessing long-lived emissive excited states continues to remain of critical importance to a variety of energy-relevant and photonics-based technologies.[1] Over the past decade, exceptional creativity has been exercised in the manipulation of chromophore electronic structures throughout the community.[2–8] Of particular interest are inorganic compounds with energetically proximate triplet excited states poised for configuration mixing and state re-ordering. For example, molecules with closely spaced triplet charge transfer (^{3}CT) and ligand-localized triplet (^{3}IL) energy levels are profoundly affected in terms of photophysical parameters relative to their parent model structures.[2,3,5,6] In 1972, Crosby and coworkers demonstrated ^{3}CT–^{3}IL configuration interactions in two different Ir(III) complexes at 77 K, cleverly modulating the triplet energy gap through variation in glass matrix.[9] In their experiments, the ^{3}CT state systematically increases as the ^{3}IL state remains fixed in energy, producing a ~7-fold lifetime difference at the extremes with no change in emission profile. While there has been some progress attempting to establish ^{3}CT–^{3}IL configuration mixing and state inversion for select molecules at room temperature,[2c,6b] no clear-cut examples of triplet state crossover have emerged to date. This is largely due to difficulties related to energy matching, electronically coupling triplet levels to facilitate strong interaction, in addition to preparing suitable model chromophores.

Recent synthetic advances coupled with explorations of molecular wire behavior in donor–bridge–acceptor (D–B–A) structures have developed the science related to conjugated bridge molecules that systematically vary in energy.[10,11] Although such tuning has been exploited to modulate singlet excited states, triplet energies are also affected to the same extent in these structures assuming the singlet–triplet gap remains constant. Together with the fact that Pt(II) diimine chromophores have solvent controllable CT energy levels,[2c,5,12] the appropriate combination of chromophores should permit the observation of solvent-induced triplet state inversion at room temperature.

With these considerations in mind, we designed compound **1** which encompasses all necessary structural elements to enable solvent-induced triplet state inversion as well as model chromophores **2** and **3** to mimic the ^{3}CT state and ^{3}IL state in **1**, respectively. Complete synthesis and structural characterization details of **1–3** are supplied as ESI.† We note that the triplet state photophysics of the related *trans*-disposed **3**, *trans*-$Pt(PBu_3)_2(PE_3)_2$ and *trans*-$Pt(PBu_3)_2(PE_3)Cl$,[13] as well as extensive studies of **2** have been reported.[2c,12] Compounds **1** and **2** purposely bear *t*-butyl groups to prevent aggregation, ensuring monomer-based photophysics and the bidentate diphosphine in **3** reproduces the *cis*-geometry of the phenyleneethynylene containing acetylide ligands (PE_3) in **1** while providing ample solubility for spectroscopic studies.

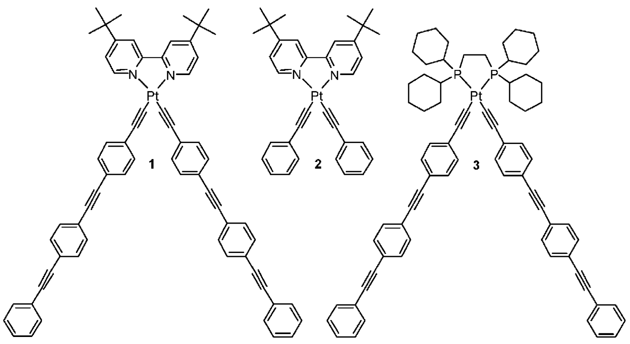

Fig. 1 presents the absorption and emission spectra of **1–3** in benzene and CH_2Cl_2. The absorption spectra of **1** and **3** possess strong π–π* absorptions from the PE_3 ligands, centered near 350 nm whereas the lower energy charge transfer

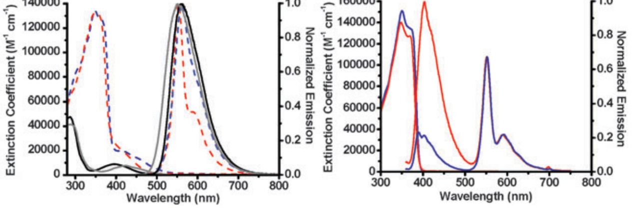

Fig. 1 (A) Absorption (leftmost data) and emission (rightmost data) spectra of **1** in deaerated benzene (dashed blue) and CH_2Cl_2 (dashed red) and **2** in deaerated benzene (black) and CH_2Cl_2 (gray). (B) Absorption (leftmost data) and emission (rightmost data) spectra of **3** in deareated benzene (blue) and CH_2Cl_2 (red).

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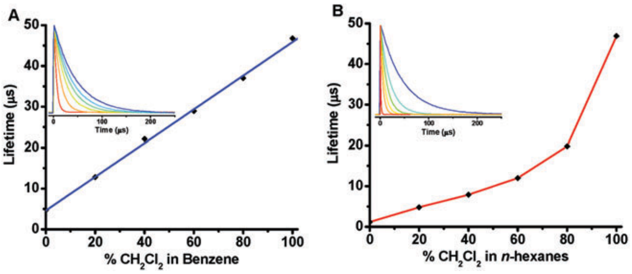

Fig. 2 The excited state lifetime of **1** (A) as a function of percent volume CH_2Cl_2 in benzene and (B) as a function of percent volume CH_2Cl_2 in *n*-hexanes. All solutions are deaerated. Insets: single exponential photoluminescence intensity decays comprising each data set.

transitions are observed as a shoulder in **1** and as a broad band in **2**. The photoluminescence from **2** is well established as ^{3}CT in nature,[2c,12] increasing in energy with solvent polarity. Similar to the related *trans*-Pt$(PBu_3)_2(PE_3)_2$, **3** displays dual emission, ligand-localized singlet fluorescence at short wavelengths in addition to triplet PE_3-based phosphorescence centered at 552 nm. The phosphorescence of **3** is completely insensitive to solvent polarity and therefore its ^{3}IL state remains fixed in energy as a function of solvent. The luminescence profile of **1** is noticeably solvent dependent, narrowing in bandshape and developing a well-defined vibronic shoulder between benzene and CH_2Cl_2. In fact the spectra of **1** and **3** measured in CH_2Cl_2 are identical in shape and possess the same excited state lifetimes within experimental error (44 and 47 µs), signaling that the emission of **1** in this solvent is most likely ^{3}IL in nature, assigned as Pt-perturbed PE_3 localized. In benzene the emission spectrum of compound **2** does not completely superimpose that of **1**, and the lifetimes significantly differ, 1.1 and 4.7 µs respectively. This is indicative of a configurationally mixed excited state in **1**, where the emission properties lie between those of **2** and **3**, *i.e.* between ^{3}CT and ^{3}IL.[2c,6b,9] Further support for triplet state configuration mixing in **1** comes from the smooth variation in emission spectra (Fig. S1†) and excited state lifetime as a function of solvent composition. This phenomenon has been previously observed by us as well as by Liu and Schanze in different metal–organic systems.[2c,6b]

Fig. 2A presents the emission lifetime of **1** measured as a function of volume percent CH_2Cl_2 in benzene; inset are the single exponential intensity decay curves which are independent of emission monitoring wavelength. The lifetimes linearly scale with CH_2Cl_2 concentration and the behavior is monotonic with a ^{3}CT–^{3}IL energy gap, between 0.08 and 0.16 eV; see Fig. S2.† Since the ^{3}CT state lies 0.08 eV (645 cm^{-1}) above the ^{3}IL state in benzene, it becomes obvious why the excited state behavior can only be characterized as ^{3}IL in CH_2Cl_2 and configuration mixed in benzene as well as CH_2Cl_2–benzene mixtures. To experimentally realize an unperturbed ^{3}CT state emission in **1**, and eventually the desired solvent-induced triplet state inversion, it is necessary to further reduce the solvent polarity to sufficiently decrease the ^{3}CT state relative to the ^{3}IL state. In pursuit of this goal, the variable solvent composition experiments were performed using mixtures of *n*-hexanes and CH_2Cl_2.

The absorption and emission spectra of **1** and **2** measured in hexanes are presented in Fig. S3.† The emission spectra of **1** and **2** are now completely superimposed and the excited state lifetimes are identical, τ = 1.1 µs, consistent with a ^{3}CT manifold. Fig. 2B illustrates the significant changes in lifetime accompanying increasing percentages of added CH_2Cl_2 in hexane solutions of **1**. In these experiments, the lifetimes and spectral changes across the solvent composition series are consistent with a complete inversion of triplet excited states in **1**, from a ^{3}CT state in hexanes to a ^{3}IL state in CH_2Cl_2. We assert that these assignments are made possible as a result of the parallel studies on **2** and **3**, which are arguably the most appropriate model chromophores. In the intermediate polarity cases, smooth transitioning of the photoluminescence data is congruent with triplet excited state configuration mixing as there is no distinct crossover observed in photophysical behavior across the series. This is also observed in the collected transient absorption data (Fig. S4†). A significant finding is that while the ^{3}CT state exerts significant perturbation on the ^{3}IL state, the opposite effect is not observed; no lifetime lengthening is seen from the ^{3}CT manifold in hexanes although the ^{3}IL state lies 0.03 eV higher in energy. This result appears to be general for many different metal–organic structures at RT and 77 K,[2c,6b–d,9] most likely having origin in the relative magnitudes of k_r and k_{nr}, where strong spin–orbit coupling associated with the ^{3}CT state leads to much larger rate constants relative to the ^{3}IL state since k_r & k_{nr} (^{3}CT) ≫ k_r & k_{nr} (^{3}IL), Table 1 and Table 2. This significant kinetic disparity results in the ^{3}CT state exerting much more influence on excited state decay parameters, in effect dominating the photophysics. In the present study, the values of k_r and k_{nr} in **1**

Table 1 Photophysical properties in deaerated solvents at room temperature

Compd	Solvent	$\lambda_{abs}{}^{a}$/nm (ε, M^{-1} cm^{-1})	$\lambda_{em}{}^{a}$ /nm	$\tau_{em}{}^{b}$ /µs	$\Phi_{em}{}^{b}$	k_{rP},^{c}/s^{-1}	$k_{nr}{}^{d}$/10^4/s^{-1}	$\Delta G_{ES}{}^{e}$ /eV
1	*n*-Hexanes	341 (133 000), 419 (19 400)	580	1.1	0.05	4.54×10^4	86.36	2.32
	Benzene	348 (134 000), 417 (19 700)	560	4.7	0.43	9.15×10^4	12.12	2.39
	CH_2Cl_2	352 (131 500), 414 (20 000)	552	46.9	0.43	0.91×10^4	1.22	2.35
2	*n*-Hexanes	289 (57 000), 440 (8000)	580	1.1	0.06	5.45×10^4	85.42	2.32
	Benzene	286 (42 200), 422 (7700)	560	1.1	0.43	39.01×10^4	51.82	2.42
	CH_2Cl_2	287 (46 100), 396 (8800)	550	1.4	0.52	37.14×10^4	34.29	2.50
3	*n*-Hexanes	347 (128 000)	396, 551	51.2	3.3×10^{-3}	64.45	1.95	2.34
	Benzene	350 (129 500)	389, 552	65.1	9.8×10^{-3}	150.53	1.52	2.34
	CH_2Cl_2	348 (129 000)	404, 552	44.2	2.4×10^{-3}	54.30	2.26	2.34

[a] Absorption and emission maxima, ±2 nm. [b] Photoluminescence quantum yields and intensity decays, ±5%. [c] $k_r = \Phi/\tau$. [d] $k_{nr} = (1 - \Phi)/\tau$. [e] Excited state energies (ΔG_{ES}) were estimated (±5%) by drawing a tangent on the high-energy side of the emission band

Table 2 Photophysical properties of **1** in varying mixtures of deaerated *n*-hexanes and CH_2Cl_2 at room temperature

% of *n*-hexanes in CH_2Cl_2	$\tau_{em}{}^a$ /μs	$\Phi_{em}{}^a$	$k_{rP}{}^b/10^4/s^{-1}$	$k_{nr}{}^c/10^4/s^{-1}$
0	46.9	0.43	0.91	1.22
20	19.8	0.38	1.91	3.13
40	12.0	0.34	2.83	5.50
60	7.9	0.26	3.29	9.36
80	4.8	0.18	3.75	17.08
100	1.1	0.05	4.54	86.36

[a] Photoluminescence quantum yields and intensity decays, ±5%. [b] $k_r = \Phi/\tau$. [c] $k_{nr} = (1 - \Phi)/\tau$

both attenuate with increasing solvent polarity and increasing ^3CT–^3IL gap, consistent with decreasing ^3CT character, Table 2.

The present study provides clear-cut experimental evidence for solvent-induced triplet state inversion at room temperature in **1**, a Pt(II) CT complex bearing two pendant PE_3 chromophores each with a low lying ^3IL manifold. The model structures **2** and **3** provide the rationale for unraveling the seemingly complex photoluminescence behavior displayed by **1**. Solvent composition systematically alters the ^3CT–^3IL energy gap which brings the two triplet states in and out of resonance, the former producing a composite excited configuration exhibiting superpositioned photophysics. A particularly attractive feature of these composite excited states is that they provide a wealth of excited state emissions and absorptions,[2c,6b] derived from the same molecule. These spectroscopic signatures can be exploited in photonics applications such as laser protection materials and extrinsic photoluminescence probes. Medium-induced control of excited state behavior in metal–organic systems is also valuable in terms of fundamental knowledge and may be exploited in a variety of research areas including adaptive quantum control[14] and solvent modulation of charge transport mechanisms.[11]

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