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ARTICLE

Heteroleptic Cationic Iridium(III) Complexes Bearing Naphthalimidyl Substituents: Synthesis, Photophysics and Reverse Saturable Absorption

Chengkui Pei, Peng Cui, Christopher McCleese, Svetlana Kilina, Clemens Burda, Wenfang Sun

Three heteroleptic cationic iridium(III) complexes containing cyclometalating 2-[3-(7-naphthalimidylfluoren-2'-yl)phenyl]pyridine ligand and different diimine (N^N) ligands (N^N = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and 5,5'-bis[7-(benzothiazol-2'-yl)fluoren-2'-yl]-2,2'-bipyridine (BTF-bpy, \( \text{Ir-3} \)) were synthesized and characterized. The photophysics of these complexes was systematically investigated via spectroscopic methods and by time-dependent density functional theory (TDDFT). All complexes possess a very weak charge-transfer tail at ca. 450 – 570 nm; and two intense absorption bands in the region of 290 – 350 nm and 350 – 450 nm, respectively. The emission of \( \text{Ir-1} \) – \( \text{Ir-3} \) in CH$_2$Cl$_2$ emanates predominantly from the C^N ligand-localized \( \pi^* \) state. These emitting excited states also give rise to broadband triplet excited-state absorption in the visible to the near-IR region (i.e. 420 – 800 nm for \( \text{Ir-1} \) and \( \text{Ir-2} \), and 460 – 800 nm for \( \text{Ir-3} \)). The kinetics of fs TA reveals that the lowest singlet excited-state lifetimes of these complexes vary from 1.43 ps to 142 ps. The stronger excited-state absorption of \( \text{Ir-1} \) – \( \text{Ir-3} \) compared to their respective ground-state absorption in the visible spectral range leads to strong reverse saturable absorption (RSA) at 532 nm for ns laser pulses. The trend of transmission signal decrease follows \( \text{Ir-2} > \text{Ir-3} > \text{Ir-1} \). Extending the \( \pi \)-conjugation of the N^N ligand increases the strength of RSA. In addition, the naphthalimidyl (NI) substitution at the C^N ligand dramatically increases the triplet excited-state lifetime and broadens the triplet excited-state absorption to the NIR region compared to the respective Ir(III) complexes with benzothiazolyl substituent on the C^N ligand.

Introduction

Octahedral $d^6$ Ru(II) and Os(II) complexes have been well studied for their photoluminescence properties. Diimine ligands (N^N), such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen), have been used for modulating the luminescence properties of the Ru(II) and Os(II) complexes in many studies. Meanwhile, tri-chelated rhodium(III) and iridium(III) complexes with diimine and / or cyclometalating bidentate ligands have also attracted much attention in the last decade. In contrast to the Rh(III) complexes that emit only at low temperature, the Ir(III) complexes demonstrate intensive phosphorescence at room temperature. In addition, a strong spin-orbit coupling admixes the singlet and triplet excited states, which increases the phosphorescence efficiency and broadens the light absorption to the longer visible and the near-IR region. The latter is due to direct absorption from the singlet ground state to the triplet excited state in iridium complexes. Therefore, the Ir(III) complexes have been widely investigated as photosensitizers for catalytic photocatalysis absorption of CO$_2$.

It is well known that the emission energy and lifetime of the heteroleptic Ir(III) complexes bearing bipiridyl (bpy, N^N ligand) and cyclometalating 2-phenylpyridine (ppy, C^N ligand) ligands could be adjusted by the electron-withdrawing or electron-donating substituents on the bpy or ppy ligands. Also, an extension of the \( \pi \)-conjugation of the N^N or C^N ligands could efficiently tune the emission energy and lifetime of the Ir(III) complexes as well. Our group has studied several series of Ir(III) complexes with a benzothiazolylfluorenyl (BTF) group attached on the N^N or C^N ligands. We found that extending the \( \pi \)-conjugation of the N^N ligand via attaching the BTF groups prolonged the lifetime of the lowest triplet excited state, while incorporating the BTF groups on the C^N ligands reduced the triplet lifetime.

The reported work on the heteroleptic cationic Ir(III) complexes is intriguing. However, studies on using the Ir(III) complexes as nonlinear optical materials has been quite limited. To date, only handful reports are found in the literature on investigating the reverse saturable absorption (RSA, i.e. the absorptivity of the material increases with the increased incident energy) of the Ir(III) complexes. It is well known that RSA has important...
applications in optical switching, optical rectification, laser pulse shaping and compression, etc. An ideal reverse saturable absorber is required to possess a large ratio of the excited-state absorption cross section with respect to that of the ground-state absorption in the visible to the near-IR region, and the excited-state lifetime should be longer than the laser pulse width. For RSA of ns laser pulses, high triplet quantum yield is another desirable feature. Developing organic or inorganic materials that can meet all these requirements have been keeping as a challenging for the nonlinear optical materials field. To realize this goal, understanding the structure-property correlation is the key.

Our previous work has also demonstrated that Pt(II) & bpy complexes bearing the naphthalimidyl (NI) group on the acetylide ligands possessed an extremely long-lived lowest triplet excited state and broaden the excited-state absorption to the near-IR region dramatically increase the lifetime of the lowest triplet excited state of the Ir(III) complexes, since NI group has been demonstrated to effect of the NI group on the C^N ligands. To illustrate the role of the NI groups and the charge transfer character of excited states in experimental data by providing additional insights into the structural DFT (TDDFT) calculations. Calculated results complement our density functional theory (DFT) and linear-response time dependent photoexcitation and emission of these complexes, we also performed the BTF-bpy ligand in Chart 1. Using the BTF-bpy ligand in Ir-3 would allow us to further demonstrate the effect of extended π-conjugation in the N^N ligand. The photophysical properties and reverse saturable absorption of these complexes were systematically investigated in order to reveal the effect of the NI group on the C^N ligands. To illustrate the role of the NI groups and π-conjugation of the C^N or N^N ligands in the photoexcitation and emission of these complexes, we also performed density functional theory (DFT) and linear-response time dependent DFT (TDDFT) calculations. Calculated results complement our experimental data by providing additional insights into the structural characteristics and the charge transfer character of excited states in Ir-1 - Ir-3.

**Experimental section**

**Synthesis and characterization**

All reagents and solvents were purchased from commercial sources and used as is unless otherwise mentioned. ^1H NMR spectra were recorded on a Varian Oxford-400 or Varian Oxford-500 spectrometer in CDCl3 with tetramethylsilane (TMS) as internal standard. High resolution mass (HRMS) analyses were performed on a Bruker BioTof III mass spectrometer. Elemental analyses were conducted by NuMega Resonance Laboratories, Inc. in San Diego, CA.

The synthetic route for Ir-1 – Ir-3 is illustrated in Scheme 1. Precursors 1,4,24, 3,38,40 and 541 were synthesized following the literature procedures. The synthesis of ligand 8 was reported by our group previously.41 The synthetic procedures and characterization data for compounds 2, 4, 6, 7 and the complexes Ir-1 – Ir-3 are reported in the following.

**Chart 1** Structures of the Ir(III) complexes Ir-1 - Ir-3.

2. Compound 1 (5.00 g, 9.16 mmol) was dissolved in 20 mL of absolute THF. The solution was degassed with argon and cooled down to -78 °C. Then 10 mL of BuLi hexane solution (2.5 M, 25 mmol) was added dropwise at -78 °C under argon atmosphere. The mixture was stirred at this temperature for 1.5 h, and 2-isopropoxy-4,4,4,5,5,5-tetramethyl-1,3,2-dioxaborolane (ITDB) (8 mL, 22.9 mmol) was added in about 15 min. The reaction mixture was allowed to gradually warm up to r.t. and stirred for overnight. 2 M HCl was added and stirred for 0.5 h to quench the reaction. The organic layer was separated and the aqueous layer was extracted with CH2Cl2 (25 mL × 2). The organic phase was combined and dried over MgSO4. The solvent was then removed under reduced pressure, and the residue was purified by elution through column chromatography (silica gel, hexane/ethyl acetate = 50/1 (v/v) was used as the eluent) to obtain product 2 as yellow oil (3.2 g, yield: 54%). ^1H NMR (CDCl3, 400 MHz) δ 0.40-0.52 (m, 8H), 0.71-0.95 (m, 2H), 1.42 (s, 2H), 1.96-2.19 (m, 4H), 7.60-7.68 (m, 2H), 7.69-7.78 (m, 2H), 7.79-7.85 (m, 2H).

4. Compounds 2 (320 mg, 0.5 mmol), 3 (96 mg, 0.3 mmol), Pd(Ph3P)4 (35 mg, 0.03 mmol), and 2 M K2CO3 aqueous solution (2 mL) were added in 10 mL toluene. The mixture was heated to reflux under argon for 24 h. After cooling down to room temperature, the
solution was concentrated in vacuum, and then extracted with CH₂Cl₂. The CH₂Cl₂ layer was washed with brine and dried over MgSO₄. The solvent was removed and the crude product was purified by column chromatography (SiO₂, hexane/ethyl acetate = 50/1 (v/v)) to get product 4 as yellow oil (110 mg, yield: 46%). ¹H NMR (CDCl₃, 400 MHz) δ 0.46-0.75 (m, 12H), 0.76-0.98 (m, 21H), 1.42 (s, 12H), 1.46-1.50 (m, 2H), 1.68-1.75 (m, 2H), 1.90-2.12 (m, 4H), 4.22 (t, J = 7.2 Hz, 2H), 7.40-7.49 (m, 2H), 7.60-7.68 (m, 2H), 7.75-7.78 (m, 1H), 7.80-7.85 (m, 3H), 8.20-8.30 (m, 1H), 8.60-8.70 (m, 2H).

Scheme 1  Synthetic route for Ir-1 - Ir-3.

6. Compounds 4 (110 mg, 0.14 mmol), 5 (46 mg, 0.20 mmol), Pd(PPh₃)₄ (30 mg, 0.02 mmol), and 2 M K₂CO₃ aqueous solution (1 mL) were added in 10 mL toluene. The mixture was heated to reflux under argon for 24 h. After cooling down to room temperature, the solution was concentrated in vacuum, and then extracted with CH₂Cl₂. The CH₂Cl₂ layer was washed with brine and dried over MgSO₄. The solvent was then removed and the crude product was purified by column chromatography (SiO₂, hexane/EA = 50/1 (v/v)) to obtain product 6 as yellow oil (60 mg, yield: 59%). ¹H NMR (CDCl₃, 400 MHz) δ 0.57-0.63 (m, 12H), 0.81-0.99 (m, 21H), 1.44-1.50 (m, 2H), 1.73-1.77 (m, 2H), 2.04-2.16 (m, 4H), 4.22 (t, J = 7.2 Hz, 2H), 7.24-7.27 (m, 1H), 7.44-7.50 (m, 2H), 7.55-7.59 (m, 1H), 7.65-7.70 (m, 5H), 7.77-7.79 (m, 2H), 7.84 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 8.25-8.30 (m, 2H), 8.63-8.67 (m, 2H), 8.73-8.74 (m, 1H). HRMS (ESI) calcd. for C₅₆H₆₃N₂O₂ (M+H): 795.4884, Found: 795.4888. Anal calcd (%) for C₅₆H₆₂N₂O₂. CH₂Cl₂.2C₆H₁₄: C, 78.75; H, 8.81; N, 2.66. Found: C, 78.38; H, 8.61; N, 3.06.

7. Ligand 6 (400 mg, 0.50 mmol) and IrCl₃H₂O (82 mg, 0.25 mmol) were dissolved in a mixture of 2-ethoxyethanol (10 mL) and
water (3 mL), and the mixture was heated at 130 °C for 24 h. After that, the mixture was cooled down to r.t. and the precipitate was collected by filtration as yellow solid. The yellow solid was washed with EtOH (20 mL) and acetonitrile (20 mL) first, and then dissolved in CH2Cl2 (25 mL). The undissolved solid was removed by filtration and methanol (30 mL) was added to the filtrate to precipitate orange solid 200 mg as compound 7.

**Ir-1.** The mixture of 7 (89 mg, 0.025 mmol), bpy (8 mg, 0.05 mmol) and AgSO3CF3 (12.5 mg, 0.05 mmol) in 2-ethoxyethanol (5 mL) and water (3 mL) was heated at 130 °C for 24 h. Then the mixture was cooled down to r.t., and NH4PF6 (16.7 mg, 0.10 mmol) was added and stirred at r.t. for 3 h. After the reaction, the solvent was removed and the residue was purified by column chromatography (CH2Cl2/ethyl acetate = 50/1 (v/v)) to yield yellow solid 50 mg (yield: 50% for two steps from ligand 6). 1H NMR (CDCl3, 400 MHz) δ 0.57-0.63 (m, 3H), 0.81-0.89 (m, 42H), 1.44-1.50 (m, 4H), 1.73-1.77 (m, 4H), 2.04-2.16 (m, 8H), 4.22 (t, J = 7.2 Hz, 2H), 6.45-6.55 (m, 2H), 7.09-7.13 (m, 2H), 7.24-7.27 (m, 2H), 7.44-7.50 (m, 6H), 7.53-7.57 (m, 10H), 7.79-7.85 (m, 6H), 8.77-9.0 (m, 2H), 8.80-8.38 (m, 4H), 8.61-8.69 (m, 6H). HRMS (ESI) calcd. for C122H130IrN6O4PF6 (M-PF6): 1936.9817. Found: 1936.9817. Anal calcld (%) for C122H130IrN6O4PF6: C, 69.54; H, 6.31; N, 3.92. Found: C, 67.09; H, 5.65; N, 3.70.

**Ir-2.** The mixture of 7 (72 mg, 0.02 mmol), 1,10-phenanthroline (7.2 mg, 0.04 mmol) and AgSO3CF3 (10 mg, 0.04 mmol) in 2-ethoxyethanol (3 mL) and water (2 mL) was heated to 130 °C for 24 h. Then the reaction mixture was cooled down to r.t., and NH4PF6 (12.5 mg, 0.04 mmol) was added and stirred at r.t. for 3 h. The solvent was removed and the residue was purified by column chromatography (CH2Cl2/ethyl acetate = 50/1 (v/v)) to get yellow solid 43 mg (yield: 47% for two steps from ligand 6). 1H NMR (CDCl3, 400 MHz) δ 0.53-0.70 (m, 28H), 0.71-1.02 (m, 38H), 1.43-1.48 (m, 4H), 1.72-1.76 (m, 4H), 1.96-2.19 (m, 8H), 4.21 (t, J = 7.2 Hz, 4H), 6.57-6.59 (m, 2H), 7.00 (t, J = 7.2 Hz, 2H), 7.32 (d, J = 7.2 Hz, 7H), 7.43-7.52 (m, 6H), 7.62-7.70 (m, 8H), 7.79-7.87 (m, 8H), 8.00-8.06 (m, 4H), 8.23-8.26 (m, 4H), 8.34-8.38 (m, 2H), 8.62-8.70 (m, 6H). HRMS (ESI) calcd. for C122H130IrN6O4PF6: 1960.9817. Found: 1960.9794. Anal calcld (%) for C122H130IrN6O4PF6: C, 69.52; H, 5.92; N, 3.80.

**Ir-3.** Complex 7 (36 mg, 0.01 mmol), ligand 8 (24 mg, 0.02 mmol) and AgSO3CF3 (10 mg, 0.04 mmol) in a mixture of 2-ethoxyethanol (3 mL) and water (2 mL) was heated to 130 °C for 24 h. Then the reaction mixture was cooled down to r.t., and NH4PF6 (12.5 mg, 0.04 mmol) was added and stirred at r.t. for 3 h. The solvent was removed and the residue was purified by column chromatography (CH2Cl2/ethyl acetate = 50/1 (v/v)) to get yellow solid 21 mg (yield: 30% for two steps from ligand 6). 1H NMR (CDCl3, 400 MHz) δ 0.42-0.98 (m, 26H), 1.44-1.49 (m, 4H), 1.73-1.78 (m, 4H), 1.86-2.19 (m, 16H), 4.22 (t, J = 7.6 Hz, 4H), 6.60-6.61 (m, 2H), 7.11-7.19 (m, 2H), 7.37 (t, J = 7.2 Hz, 4H), 7.41-7.58 (m, 8H), 7.60-7.80 (m, 14H), 7.81-7.89 (m, 8H), 8.10-8.18 (m, 10H), 8.25-8.31 (m, 2H), 8.42-8.56 (m, 4H), 8.85 (t, J = 7.6 Hz, 4H), 8.84-8.92 (m, 2H). HRMS (ESI) calcd. for C194H121IrN6O5S2PF64CHCl3: C, 66.01; H, 6.16; N, 3.11. Found: C, 66.08; H, 5.75; N, 3.25.

**Photophysical measurements.** The spectrophotometric grade solvents used for photophysical experiments were purchased from VWR International and used as is. A Shimadzu UV-2501 spectrophotometer was used to record the UV–vis absorption spectra in different solvents. An HORIBA FluoroMax 4 fluorometer/phosphorometer was utilized to measure the steady-state emission spectra in different solvents. The emission quantum yields were determined by the relative actinometry method in degassed solutions, in which a degassed CH3CN solution of [Ru(bpy)]2Cl2 (Φem = 0.097, λex = 436 nm) was used as the reference for Ir-1 – Ir-3, and a 1 N sulfuric acid solution of quinine bisulfate (Φem = 0.546, λex = 374.5 nm) was used as the reference for ligands 6.

The nanosecond transient difference absorption (TA) spectra and decays were measured in degassed CH2Cl2 solutions on an Edinburgh LP920 laser flash photolysis spectrometer. The third harmonic output (355 nm) of a Nd:YAG laser (Quantel Brilliant, pulse width = 4.1 ns, repetition rate = 1 Hz) was used as the excitation source. Each sample was purged with argon for 45 min prior to measurement. The triplet excited-state absorption coefficient (εT) at the TA band maximum was determined by the singlet depletion method, in which the following equation was used to calculate the εT:

$$\epsilon_T = \frac{\epsilon_s [\Delta OD_s]}{\Delta OD_T}$$

where εs is the ground-state molar extinction coefficient at the wavelength of the bleaching band minimum of the TA spectrum; ΔODs and ΔODT are the optical density changes at the minimum of the bleaching band and the maximum of the positive absorption band, respectively. After obtaining the εT value, the triplet quantum yield (ΦT) could be determined by the relative actinometry. The ΔOD of an optically matched sample solution at the excitation wavelength of 355 nm in a 1-cm cuvette was compared to that of the reference solution (SiNc in benzene) at 590 nm (ε590 = 70,000 L mol−1 cm−1, ΦT = 0.20) using equation (2) to calculate the ΦT:

$$\Phi_T = \frac{\epsilon_T^s x \Delta OD_T^T}{\epsilon_T^s x \Delta OD_s^T}$$

where the superscript s represents the samples, ΔOD is the optical density change at 590 nm, and εT is the triplet excited-state extinction coefficient.

The femtosecond laser pump–probe system consists of an amplified erbium-doped fiber laser, which is frequency doubled to 780 nm and amplified in a regenerative amplifier (Clark MXR CPA 2001). This femtosecond laser produces pulses with 120 fs FWHM duration and 800 mJ output energy per pulse at a repetition rate of 1 kHz. A small portion of the fundamental output pulse train is used to generate white light in a 2 mm sapphire crystal while the remaining laser light is used to frequency-double the 780 nm light in order to achieve 390 nm. For the femtosecond laser spectroscopy measurements, the excitation beam was modulated by a chopper with a 100 Hz frequency. The probe light was used with reflective optics in order to avoid white light dispersion. Measurements were
conducted with the excitation beam focused to a spot diameter of about 1 mm and the probe beam to 200 μm. For measurements in this study, the sample solutions were placed in a 2-mm path length quartz cuvette. Absorption spectra of Ir-1 – Ir-3 and ligand 6 were taken before and after the time-resolved experiment and no significant change was observed. All fs TA measurements were performed at room temperature.51–57

Nonlinear transmission experiment.

The reverse saturable absorption of Ir-1 – Ir-3 was characterized by a nonlinear transmission experiment at 532 nm using a Quantel Brilliant laser as the light source. The pulse width of the laser was 4.1 ns, and the repetition rate was set to 10 Hz. The complexes were dissolved in CH2Cl2 and the concentration of the sample solutions (CPCM)62,63 implemented in Gaussian 09. Including solvent also property calculations were performed in dichloromethane chemistry software package.58 The hybrid PBE159 functional was response TDDFT, as implemented in Gaussian 09 quantum optimized at the level of DFT, while the excited-state properties, radius of the beam waist at the focal point was approximately 96 μm.

The ground-state geometries of Ir-1 – Ir-3 and ligand 6 were optimized at the level of DFT, while the excited-state properties, including absorption and emission, were calculated using linear response TDDFT, as implemented in Gaussian 09 quantum chemistry software package.58 The hybrid PBE159 functional was chosen to optimize the ground state geometry, which incorporates PBE nonlocal exchange and 25% of the local Hartree Fock (HF) exchange. For all calculations, the LANL2DZ basis set60 was applied for heavy Ir ion, while the remaining atoms were modeled by 6-31G* basis set.51 Both geometry optimization and optical property calculations were performed in dichloromethane (CH2Cl2, eν = 9.08) using the conductor polarized continuum model (CPCM)62,63 implemented in Gaussian 09. Including solvent also helps to remove the spurious charge transfer states, a well-known problem of TDDFT.64,65

Our previous work demonstrates that the chosen methodology allows for accurate enough representations of the ground- and excited-state properties of various Ir(III) complexes.35 We have found that optimized geometries of Ir-1 – Ir-3 negligibly depend on the functional used in calculations. However, the excited states properties are highly sensitive to the percentage of the HF local exchange in the functional,40 leading to either a blue-shift of the excited energy for the high-portion of HF in the functional or a red-shift for lower percentage of the HF, as compared to the experimental spectra. Therefore, we changed the HF portion in PBE1 functional to 31%, which provided the best agreement with the experimental spectra of all complexes we studied. To keep consistency, the same 31% percentage of HF was also used in the subsequent calculations of the emission energies. Interestingly, despite a constant shift of excited energies, the choice of a functional and a portion of the HF exchange in it insignificantly affect the nature of orbitals contributing to optical transitions.

For absorption spectral calculations, 40 lowest singlet excited states were calculated to reproduce the experimental spectra in the 250-600 nm range. The discrete optical transitions with their corresponding oscillator strength were broadened by a Gaussian function with the line width of 0.08 eV to represent an experimental inhomogeneous spectral broadening. To obtain the triplet (phosphorescence) and singlet (fluorescence) emission energies, the molecular structures of the lowest singlet excited (S₁) and lowest triplet excited (T₁) states were optimized using analytical TD-DFT gradients,57,68 as implemented in the Gaussian 09 software. A compact representation of an excited state via photoexcited electron-hole pair, which fits for chemical intuition, can be obtained using natural transition orbitals (NTOs).69,70 By performing NTO calculations implemented in Gaussian 09, a single particle transition from a ground state to an excited state could be generated through unitary transformation of transition density matrix of a specific excited state, which provides an excited hole (occupied NTO) and an electron (unoccupied NTO).69 For visualizing NTOs pairs contributing to the most important optical transitions, Chemcraft-1.7 software71 was used for plotting excited charge densities by setting iso value as 0.02.

Computational methods

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Results and discussion

Molecular geometries

The optimized ground-state geometries of Ir-1 – Ir-3 in CH2Cl2 at the DFT level of theory are presented in ESI Figure S1. The dihedral angles between the different parts in the C^N and N^N ligands for Ir-1 – Ir-3 are listed in ESI Table S1. Although in principle three configurations are possible for the Ir(ppy)2(bpy)+ type molecules (see Chart 2),72 it is well known that configuration A with the two cyclometalating carbons cis to each other and coplanar with the two nitrogen atoms on the diimine ligand is the commonly formed one.70,73,74,75 Therefore, although we don’t have the crystal structures to confirm the configurations of Ir-1 – Ir-3, the 1H-NMR spectra provided in ESI Figure S2 manifest the existence of only one isomer in our product. We believe it is reasonable to assume that Ir-1 – Ir-3 adopt the configuration of A. The same configuration was used for our DFT calculations.

Chart 2 Possible configurations for Ir(ppy)2(bpy)+ type molecules

For optimization of the ground-state geometry of Ir-1 – Ir-3, we started from planar structures for all complexes. However, upon optimization, the fluorenyl substituents at the 2-phenylpyridine (C^N) ligands are twisted from the 2-phenylpyridine plane by ~35–38°, which are similar to those reported for the other Ir(III) complexes bearing the BTF substituted C^N ligands.35,37,76 The NI substituents attached at the 7-position of the fluorenyl motif are also

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twisted from the fluorene plane by an angle of ~ 50-53°, which are
dramatically different from the dihedral angles between the
benzothiazolyl substituent and the fluorenyl motif (~0°-2°) in the
other Ir(III) complexes bearing the BTF substituted C^N
ligands.\(^3,5,7\,\) In Ir-3, the fluorenyl substituents attached at the 5,5-
positional of the bpy ligand deviate from the bpy plane by an angle of
~ 34°, and the benzothiazolyl substituents exhibit a dihedral angle of
< 1° with respect to the fluorene plane, due to geometry
optimization.

**UV-vis absorption**

The UV-vis absorption spectra of Ir-1 – Ir-3 and the ligand 6 in a
CH\(_2\)Cl\(_2\) solution (1x10\(^{-5}\) mol/L) are depicted in Figure 1(a) and are
compared to the calculated absorption spectra in Figure 1(b). More
detailed information on the absorption band maxima and extinction
coefficients are listed in Table 1. The calculated spectra well
reproduce the two dominant absorption bands revealed in the
experimental data. Both of these bands well correlate with the main
absorption bands of ligand 6 (dark cyan line in Figure 1(a)). Excited-
state orbitals, i.e. the natural transition orbitals (NTOs),
corresponding to the most intensive optical transitions demonstrate
that the lowest-energy transition of 6 has a hole being mostly
localized on the phenylfluorene component and an electron
predominantly located on the NI group (see Table 2). Therefore,
the lowest-energy band (ca. 380 nm) of 6 has the predominant
intraligand charge transfer (1ILCT) character. Optical transitions
contributing to the high-energy absorption band (ca. 296 nm) hold
mostly the delocalized 1\(\pi\pi^*\) character with some admixture of
1ILCT features (see NTOs for the 4\(^{th}\) and 5\(^{th}\) excited states in Table
2). As such, it is reasonable to assume that both optically intensive
bands in 1Ir-1 – 1Ir-3 are also dominated by the 1ILCT or 1\(\pi\pi^*\)
characters. Compared to ligand 6, however, the absorption bands of
Ir(III) complexes exhibit a bathochromic shift, which is more salient
in complex 3. Such a red-shift is caused by the delocalization of the
ligand-center \(\pi\) orbitals facilitated by the Ir(III) \(d\) orbitals.\(^7\)

In addition, the interactions between the ligands and the Ir(III)
ion result in the appearance of the lowest energy optical transitions
that contribute to the shoulder in the range of ca. 450-570 nm (see
insert of Figure 1(a)). Optical transitions contributing to this
shoulder predominantly arises from the hole that is hybridized over
Ir(III) \(d\)-orbital and \(\pi\)-orbital of the C^N ligands to the \(\pi^*\) electron
mostly localized on the N^N ligand, as depicted by NTOs presented
in Table 3. Thus, the lowest transitions of 1Ir-1 – 1Ir-3 are
attributed to ligand-to-ligand charge transfer (1LLCT) / metal-to-ligand charge
transfer (1MLCT) in nature. Because the most extended \(\pi\)-
conjugation of the BTF-bpy ligand in Ir-3 stabilizes the bpy
localized \(\pi^*\) orbital compared to those in Ir-1 and Ir-2, the lowest
energy 1MLCT/1LLCT transitions are more red-shifted in Ir-3.

As demonstrated in Figure 1(a), the intensive low-energy
absorption bands at ca. 380-400 nm for 1Ir-1 – 1Ir-3 feature the
similar shape and energy to that of ligand 6. Thus, it is reasonable
to assume that these bands have the similar nature as that for ligand 6,
namely predominantly 1ILCT transitions from the phenylfluorene to
NI component in the C^N ligand with admixture of minor 1\(\pi\pi^*\)
(\(\pi\)(NI) \(\rightarrow\) \(\pi^*\)(NI)) character, as discussed earlier for ligand 6. This
notion is supported by the NTOs illustrated in Table 4. However,
NTOs in Table 4 reveal that contribution of 1MLCT (d(Ir) \(\rightarrow\)
\(\pi^*\)(NI)) transition is also noticeable in these absorption bands.

Contribution of both types of transitions (1ILCT/1\(\pi\pi^*\) and 1MLCT)
at the same energy interval increases the intensity and broadens the
main low-energy absorption band, as compared to that in ligand 6. In
Ir-3, the intensive transitions at ca. 404 nm hold a predominant
1\(\pi\pi^*/1\pi^*\) (\(\pi\)(BTF) \(\rightarrow\) \(\pi^*\)(bpy)) character localized on the N^N
ligand in addition to the 1ILCT/1\(\pi\pi^*/1MLCT transitions based on the
C^N ligand. The predominant contribution of the N^N ligand
localized 1\(\pi\pi^*/1\pi^*\) transitions to the low-energy absorption band in
Ir-3 causes a significant red-shift and enhanced intensity of this
band in comparison to the respective bands in Ir-1 and Ir-2. Similar
effect has been observed in Pt(II) complexes bearing BTF functionalized
bpy ligand.\(^3\)

![Fig. 1](image_url)

**Fig. 1** The experimental (a) and calculated (b) UV-vis absorption
spectra of complexes Ir-1 – Ir-3 and ligand 6 in CH\(_2\)Cl\(_2\). The inset
in (a) is the expanded experimental spectra between 450 and 600 nm.

The other major absorption band at ca. 325 nm (experiment) in
Ir-1 – Ir-3 (which corresponds to the calculated – 304 – 310 nm
transitions) is dominated by the 1\(\pi\pi^*\) transitions associated with the
C^N ligand, as illustrated by the NTOs in Table 5. These 1\(\pi\pi^*\)
transitions also have some admixture of 1\(\pi\pi^*/1MLCT\) characters,
since an electron is partially delocalized over the N^N ligands, while
the hole is hybridized with \(d\)-orbital of the Ir(III). Additionally, very
minor signature of 1ILCT transition from the phenylfluorene
component to the NI component or the pyridine ring of the C^N
ligand is evident. In addition to this major absorption band, Ir-3 has a salient shoulder at ca. 350 nm (corresponding to the calculated ~325 nm transitions), which contains the prevailing \(^1\pi\pi^*\) character originating from the NI component and the \(^1\text{ILCT}\) character from the phenylfluorene component to the NI component. A minor \(^1\text{LLCT}/\text{MLCT}\) contribution is also evident for these transitions. The predominant \(^1\pi\pi^*/\text{ILCT}\) nature of excited orbitals contributing to this shoulder in Ir-3 explains the higher intensity of the high-energy absorption band of Ir-3 compared to the other two complexes.

Table 1 Photophysical data of Ir-1 – Ir-3 and ligand 6.

<table>
<thead>
<tr>
<th></th>
<th>(\lambda_{\text{abs}}/\text{nm} (\epsilon/10^3 \text{ L mol}^{-1} \text{ cm}^{-1}))</th>
<th>(\lambda_{\text{em}}/\text{nm} (\Phi_{\text{em}}; \kappa_{\text{em}}/\text{L mol}^{-1} \text{ s}^{-1}))</th>
<th>(\lambda_{T1-T0}/\text{nm} (\Phi_{T1}; \kappa_{T1}/10^4 \text{ L mol}^{-1} \text{ cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-1</td>
<td>311 (12.49), 324 (13.04), 383 (8.24)</td>
<td>606 (9.5; 4.75\times10^5; 0.081)</td>
<td>592</td>
</tr>
<tr>
<td>Ir-2</td>
<td>311 (10.74), 325 (12.70), 381 (7.58)</td>
<td>600 (41.1; 5.10\times10^5; 0.15)</td>
<td>592</td>
</tr>
<tr>
<td>Ir-3</td>
<td>306 (13.75), 323 (15.11), 404 (12.87)</td>
<td>609 (2.2; -; 0.18)</td>
<td>594</td>
</tr>
<tr>
<td>6</td>
<td>296 (8.08), 319 (6.99), 380 (5.07)</td>
<td>498 (-; -; 0.60)</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^{a}\)Absorption band maxima and molar extinction coefficients in CH\(_2\)Cl\(_2\) at room temperature. \(^{b}\)Room temperature emission band maxima, intrinsic lifetimes, self-quenching rate constants and emission quantum yields measured in CH\(_2\)Cl\(_2\). A degassed CH\(_3\)CN solution of [Ru(bpy)\(_3\)]Cl\(_2\) (\(\Phi_{\text{em}} = 0.097, \lambda_{\text{em}} = 436 \text{ nm}\)) was used as the reference. \(^{c}\)Calculated by TDDFT for optimized triplet geometry. \(^{d}\)Nanosecond transient absorption band maxima, triplet extinction coefficients, triplet excited-state lifetimes and quantum yields measured in CH\(_2\)Cl\(_2\) at room temperature. SiNc in C\(_6\)H\(_6\) was used as the reference. (\(\epsilon_{590 \text{ nm}} = 70,000 \text{ L mol}^{-1} \text{ cm}^{-1}\); \(\Phi_T = 0.20\)).

Table 2 Natural transition orbitals (NTOs) representing the main absorption bands of ligand 6.

<table>
<thead>
<tr>
<th>Excited states and properties</th>
<th>Hole</th>
<th>Electron</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_1) 385 nm (f = 0.765)</td>
<td>79%</td>
<td>79%</td>
</tr>
<tr>
<td>(S_2) 320 nm (f = 0.141)</td>
<td>16%</td>
<td>16%</td>
</tr>
<tr>
<td>(S_3) 297 nm (f = 0.129)</td>
<td>16%</td>
<td></td>
</tr>
<tr>
<td>(S_3) 296 nm (f = 0.992)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The UV-vis absorption of Ir-1 – Ir-3 and ligand 6 in toluene, acetonitrile and acetone are also studied to evaluate the solvent dependency of the optical transitions of Ir-1 – Ir-3 and to confirm our aforementioned assignments for the absorption bands. These results are provided in ESI Figures S4-S7. The results manifest that the polarity of solvent negligibly affects the transition energies of these complexes and ligand. This phenomenon can be accounted for by the mixed nature of various charge transfer transitions and \(^1\pi\pi^*\) transitions in the two major absorption bands.

Table 3 Natural transition orbitals (NTOs) representing the lowest energy transitions contributing to the shoulder of the 380 - 400 nm band of Ir-1 – Ir-3.

<table>
<thead>
<tr>
<th>Excited states and properties</th>
<th>Hole</th>
<th>Electron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-1 (S_1) 447 nm (f = 0.0005)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir-2 (S_1) 442 nm (f = 0.0011)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir-3 (S_1) 473 nm (f = 0.0068)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4 Natural transition orbitals (NTOs) representing the main low-energy absorption bands (380 – 400 nm) of Ir-1 – Ir-3.

<table>
<thead>
<tr>
<th>Excited state and properties</th>
<th>Hole</th>
<th>Electron</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ir-1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S_2 ) ( 394 \text{ nm} ) ( f = 0.895 )</td>
<td><img src="image1" alt="" /></td>
<td><img src="image2" alt="" /></td>
</tr>
<tr>
<td>( S_3 ) ( 392 \text{ nm} ) ( f = 0.719 )</td>
<td><img src="image3" alt="" /></td>
<td><img src="image4" alt="" /></td>
</tr>
<tr>
<td><strong>Ir-2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S_1 ) ( 395 \text{ nm} ) ( f = 0.830 )</td>
<td><img src="image5" alt="" /></td>
<td><img src="image6" alt="" /></td>
</tr>
<tr>
<td>( S_4 ) ( 393 \text{ nm} ) ( f = 0.793 )</td>
<td><img src="image7" alt="" /></td>
<td><img src="image8" alt="" /></td>
</tr>
</tbody>
</table>

Table 5 Natural transition orbitals (NTOs) representing the high-energy major absorption bands of Ir-1 – Ir-3.

<table>
<thead>
<tr>
<th>Excited states and properties</th>
<th>Hole</th>
<th>Electron</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ir-1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S_{17} ) ( 310 \text{ nm} ) ( f = 1.129 )</td>
<td><img src="image9" alt="" /></td>
<td><img src="image10" alt="" /></td>
</tr>
<tr>
<td>( S_{20} ) ( 304 \text{ nm} ) ( f = 0.749 )</td>
<td><img src="image11" alt="" /></td>
<td><img src="image12" alt="" /></td>
</tr>
<tr>
<td><strong>Ir-2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S_{25} ) ( 307 \text{ nm} ) ( f = 0.772 )</td>
<td><img src="image13" alt="" /></td>
<td><img src="image14" alt="" /></td>
</tr>
</tbody>
</table>

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Photoluminescence

The normalized room-temperature emission spectra of Ir-1 – Ir-3 and ligand 6 in CH₂Cl₂ are shown in Figure 2, and the emission data are summarized in Table 1. Ligand 6 exhibits intense fluorescence in CH₂Cl₂ with the band maximum at 498 nm; while Ir-1 – Ir-3 exhibit much red-shifted emission at room temperature with the band maximum at 606 nm, 600 nm and 609 nm, respectively. The emission of Ir-1 – Ir-3 shows a significant red-shift with respect to their excitation wavelengths, and the emission lifetimes in argon saturated CH₂Cl₂ solutions are in the range of 2.2 - 41.1 µs (see Table 1). The dramatic red-shift and long lifetime of the emission of Ir-1 – Ir-3 suggest phosphorescence nature of the emission from these complexes. However, despite the different diimine ligands in these complexes, the emission energies of Ir-1 – Ir-3 are quite similar. This implies that the emission of Ir-1 – Ir-3 probably originates from the same structural component, likely the substituted C^N ligands.

This assumption is confirmed by the calculated NTOs contributing to the lowest-energy triplet transition, as depicted in Table 6. All complexes have the lowest energy triplet state of the exclusive 3π,π* character associated with the fluorenlynapthalimide component at one of the C^N ligands. In contrast, the lowest-energy singlet state of Ir-1 and Ir-3 has the 1LLCT/1MLCT character with the electron being mostly located at the N^N ligand, and the hole being delocalized on the phenylfluorene motif of the C^N ligand and on the d-orbital of the Ir(III) ion. For Ir-2, the lowest-energy singlet state has the predominant fluorenlynapthalimide localized 1π,π* character with some admixture of 1MLCT/1ILCT characters. The splitting between the singlet and triplet states is the largest for Ir-2 and is the smallest for Ir-3. This feature along with the different origins of the lowest singlet excited state for Ir-2 and Ir-3 may explain the dramatically different emission lifetimes of Ir-2 and Ir-3 due to a weaker mixture between the singlet and triplet states in Ir-2 but a stronger mixture in Ir-3 when spin-orbit coupling is taking into account.

To further understand the nature of the emission in Ir-1 – Ir-3 and ligand 6, the emission of these compounds is studied in different solvents. As shown in ESI Figure S8 and Table S3, ligand 6 shows a positive solvatochromic effect when the polarity of the solvent increases. This is consistent with the 1MLCT/1π,π* nature (see the calculated NTOs contributing to the lowest-energy singlet transition depicted in ESI Table S4, which shows a major contribution from...
the 1ILCT transition) of the fluorescence for ligand 6. In contrast, the emission spectra of Ir-1 – Ir-3 demonstrate a minor solvatochromic effect in different solvents as shown in ESI Figures S9-S11 and Table S3. This is consistent with the 3π,π* nature for the emission of these complexes.

The emission of complexes at room temperature is concentration dependent. Although the emission intensity keeps increasing in the concentration range of 2×10^{-6} to 1×10^{-4} mol/L for Ir-1 and Ir-2, as shown in ESI Figures S12 and S13, the emission lifetime keeps decreasing with increased concentration. This indicates the occurrence of self-quenching in the concentration range studied for these two complexes. The self-quenching rate constants are deduced from the slopes of the Stern-Volmer plots and listed in Table 1. For Ir-3, the emission intensity increases in the concentration range of 2×10^{-6} to 1×10^{-5} mol/L, but decreases when the concentration is higher than 1×10^{-5} mol/L (see ESI Figure S14). However, the lifetime remains the same at different concentrations, implying the absence of self-quenching in Ir-3. This can be explained by the additional branched alkyl groups on the substituted N^N ligand, which help reduce the intermolecular interactions and prevent self-quenching. Considering the distinctively higher ground-state absorption at the excitation wavelength (λex = 450 nm) for Ir-3, the observed decrease of the emission intensity at high concentrations should emanate from the inner-filter effect, which could also present in Ir-1 and Ir-2, but with a much smaller effect because of the much smaller molar extinction coefficients at 450 nm for Ir-1 and Ir-2 compared to that of Ir-3.

![Normalized emission spectra of Ir-1 – Ir-3 (λex = 450 nm) and ligand 6 (λex = 379 nm) in CH2Cl2 solutions (c = 1 × 10^{-5} mol/L) at room temperature.](image)

**Table 6** NTOs contributing to the photoluminescence transitions corresponding to the lowest triplet excited-state energies and lowest singlet excited-state energies for Ir-1 – Ir-3.

<table>
<thead>
<tr>
<th></th>
<th>T_1 (nm)</th>
<th>Electron</th>
<th>Hole</th>
<th>S_1 (nm)</th>
<th>Electron</th>
<th>Hole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-1</td>
<td>592</td>
<td></td>
<td></td>
<td>557</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir-2</td>
<td>592</td>
<td></td>
<td></td>
<td>482</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir-3</td>
<td>594</td>
<td></td>
<td></td>
<td>575</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Transverse absorption (TA)**

Many heteroleptic Ir(III) complexes have been reported to possess broad and moderately strong triplet excited-state absorption in the visible to near-IR region, which is an important feature for an ideal reverse saturable absorber. To evaluate the feasibility of Ir-1 – Ir-3 as potential reverse saturable absorbers, the excited-state absorption spectra, the excited-state lifetimes and the triplet excited-state quantum yields should be assessed. Therefore, the ns and fs transient absorption (TA) spectra of these complexes and ligand have been investigated.
The nanosecond TA spectra of **Ir-1** – **Ir-3** and ligand **6** at zero delay after excitation in degassed CH₂Cl₂ solutions are illustrated in Figure 3, and the time-resolved spectra are provided in the Supporting Information Figures S16-19. The TA spectrum of ligand **6** features two major absorption bands, a stronger one between 400 and 600 nm and a weaker but much broader one above 600 nm. In addition, bleaching occurs between 360 and 400 nm, which coincides with the 1ILCT band in its UV-vis absorption spectrum. Compared to the TA spectrum of the ligand, the spectra of **Ir-1** – **Ir-3** exhibit similar features but with an obvious red-shift, indicating electron delocalization induced by the interaction of the Ir(III) center with the ligand. For all complexes, bleaching occurs at λ < 425 nm, which is consistent with the position of the low-energy major absorption band in their respective UV-vis absorption spectrum. The triplet lifetimes deduced from the decay of the TA (Table 1) for these complexes are similar to those obtained from the decay of emission, suggesting that the observed TA could arise from the same excited state that emits or an excited state that is in equilibrium with the emitting state. Considering the similar features of the TA of these complexes to that of the ligand and the similar lifetimes to those of emission, we tentatively assign the observed TA to the C^N ligand localized 3π,π* state.

One point worthy of mention is that the TA spectrum of **Ir-2** is much broader (see the comparison in ESI Figure S20) and long-lived (τₚ = 41.5 μs in CH₂Cl₂) in comparison to that of its corresponding Ir(III) complex with benzothiazolyl substituent on the C^N ligand (i.e. complex 4 in reference 37 with τₚ = 12.9 μs in CH₂Cl₂ and τₚ = 11.3 μs in toluene).37 The similar phenomenon has been reported for the Pt(II) complexes with naphthalimidyl substituted fluorenylacetylide ligands.40

![Fig. 3](image_url)

**Fig. 3** Nanosecond transient differential absorption spectra of **Ir-1** – **Ir-3** and ligand **6** in degassed CH₂Cl₂ solution at zero time delay after excitation. λₑₓ = 355 nm, A₅₃₅ nm = 0.4 in a 1-cm cuvette.

To further understand the singlet excited-state characteristics, femtosecond TA spectra and kinetics of **Ir-1** – **Ir-3** and ligand **6** were investigated. The time-resolved TA spectra of **Ir-1** and the decay profile at 675 nm are illustrated in Figure 4. Right after the 390 nm excitation (i.e. at 0.2 ps delay), the complex exhibits a broad transient absorption with band maxima at 550 nm and 675 nm, respectively. Then, the 550 nm band rapidly decays within 1 ps and blue-shifts to 515 nm, accompanied by the increase and a slight red-shift of the 675 nm band. At approximately 1.3 ns after excitation, the TA signals reach the maximum. After that, the TA decays slowly, and the shape of the TA spectrum resembles that of the ns TA spectrum. Fitting of the kinetics at 675 nm reveals that this complex possesses a rapid decay of 1.55±0.28 ps, a rise time of 142±22 ps, and a long-lived component that could not be fitted within the first 3 ns. Considering the nature of the 390 nm band as discussed in the previous section, we tentatively attribute the initial rapid decay to the decay of the 1ILCT state to the lowest singlet excited state (1ILCT/1MLCT); while the 142 ps lifetime could be ascribed to the decay of the 1ILCT/0MLCT state including intersystem crossing to the 1π,π* state. The longer lifetime that exceeds the limit of the fs TA spectrometer should be due to the decay of the triplet excited state. **Ir-2** exhibits the similar spectral features and kinetics as those of **Ir-1** (see ESI Figure S21), with a rapid decay of 1.03±0.14 ps, a rise time of 135±18 ps, and a long-lived component of > 3 ns.

In contrast to **Ir-1** and **Ir-2**, the fs TA spectrum of **Ir-3** (Figure S22 of ESI) does not show any observable changes within the first 3 ns, with a rise time of 1.43±0.25 ps and a long-lived component when monitored at 536 nm. The TA spectral feature is similar to that of the ns TA spectrum. This implies that the intersystem crossing of **Ir-3** is ultrafast, probably due to the smaller separation between the lowest singlet and triplet excited states in this complex compared to those in **Ir-1** and **Ir-2**.
Fig. 4 (a) Femtosecond time-resolved TA spectra of Ir-1 in CH2Cl2. The sample was excited with 390 nm and a power of 0.61 mW. (b) Normalized fs TA kinetics of Ir-1 at 675 nm. The inset shows the fit of the initial decay within the first 20 ps after excitation.

Reverse saturable absorption (RSA)
The fs and ns TA show that Ir-1 – Ir-3 all possess stronger excited-state absorption than that of the ground state at 532 nm, as manifested by the positive absorption at this wavelength. Meanwhile, the triplet excited-state lifetimes for these complexes are much longer than the nanosecond laser pulse width (4.1 ns). These features provide the necessary conditions for RSA to occur for a nanosecond laser pulse at 532 nm. To verify this, nonlinear transmission experiments were conducted for Ir-1 – Ir-3 in CH2Cl2 solutions at a linear transmittance of 90% in a 2-mm cuvette using 4.1 ns, 532 nm laser pulses. The results are shown in Figure 5. When the incident energy increases, all of the complexes exhibit remarkable transmission decrease, indicative of the occurrence of strong RSA. The strength of the transmission decrease follows this trend: Ir-2 > Ir-3 > Ir-1.

To rationalize the observed transmission decrease trend for Ir-1 – Ir-3, the key parameters that determine the strength of RSA for ns pulses at 532 nm, i.e. the triplet quantum yield and the ratio of the excited-state absorption cross section to that of the ground state (σex/σg), have to be evaluated. The detailed procedure for estimation of the σex/σg values of Ir-1 – Ir-3 follows that described by our group previously.35,41 The σg values at 532 nm can be calculated from the ground-state absorption molar extinction coefficients (ε) using equation σ = 3.82 × 10^{−21}ε. The σex value at 532 nm can be estimated from the ΔOD of the ns TA at zero time delay at 532 nm and at the TA band maximum (λ_{T1–Tn}), the ground-state absorbance (A) at 532 nm and at the TA band maximum of the same solution used for the TA measurement, and the ε(T1–Tn) at the TA band maximum, as well as the conversion equation σ = 3.82 × 10^{−21}ε. The obtained σex and σg values as well as the ratios of σex/σg are listed in Table 7. For RSA of ns laser pulses, the triplet quantum yield ΦT also plays an important role in the triplet excited-state absorption. Therefore, the combined ratios of ΦTσex/σg for Ir-1 – Ir-3 should be taken into account. As listed in Table 7, the ΦTσex/σg values correlate with the observed trend of the transmission signal decrease for Ir-1 – Ir-3 very well. A more quantitative analysis of the RSA results and comparison to the other reported reverse saturable absorbers require a Z-scan study, which will be carried out in the future. Nonetheless, this preliminary study demonstrates that Ir-1 – Ir-3 exhibit strong RSA at 532 nm. Considering their broadband excited-state absorption in the visible to the near-IR region and the long-lived triplet excited states, these complexes could potentially be used as broadband reverse saturable absorbers, both spectrally and temporally. This result also indicates that extending the π-conjugation of the N’N ligand could enhance the RSA of the Ir(III) complexes, as manifested by the slightly stronger RSA of Ir-2 and Ir-3 in comparison to that of Ir-1.

Fig. 5 Transmittance vs. incident energy curves for Ir-1 – Ir-3 in CH2Cl2 for 4.1 ns laser pulses at 532 nm in a 2-mm cuvette. The linear transmission was adjusted to 90% for each sample in the 2-mm cuvette. The radius of the beam waist at the focal point was ~96 μm.

Table 7 Ground-state (σg) and excited-state (σex) absorption cross sections of Ir-1 – Ir-3 in CH2Cl2 at 532 nm.

<table>
<thead>
<tr>
<th>Complex</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>σg/10^{-18} cm²</td>
<td>1.91</td>
<td>0.64</td>
<td>2.55</td>
</tr>
<tr>
<td>σex/10^{-18} cm²</td>
<td>496</td>
<td>596</td>
<td>289</td>
</tr>
<tr>
<td>σex/σg</td>
<td>260</td>
<td>931</td>
<td>113</td>
</tr>
<tr>
<td>ΦTσex/σg</td>
<td>9.6</td>
<td>32</td>
<td>10</td>
</tr>
</tbody>
</table>

Conclusions
Three new Ir(III) complexes with cyclometalating 2-[3-(7-naphthalimidyldifluorene-2-yl)phenyl]pyridine ligands were synthesized and their photophysical properties were systematically investigated. All complexes have two strong absorption bands between 290 nm and 450 nm, with the low-energy band (350 – 450 nm) predominantly from the 1ILCT (π(phenylfluorene) → π*(NI)) / 1π,π* (π(NI) → π*(NI)) / 1MLCT (d(Ir) → π*(NI)) transitions but...
admixing with $^{1}\pi^{n}\pi$ ($\pi$(bpy) $\rightarrow$ $\pi^{n}$(bpy)) / $^{1}\text{ILCT}$ ($\pi$(benzothiazolylfluorene) $\rightarrow$ $\pi^{n}$(bpy)) configurations in Ir-3. Due to the involvement of the $^{1}\pi^{n}\pi$/ILCT transitions, the low-energy band of Ir-3 is much broader, red-shifted and more intense than the corresponding bands in Ir-1 and Ir-2. The high-energy main absorption bands at ~320 nm for Ir-1 – Ir-3 are dominated by the C$^{N}$ ligand-localized $^{3}\pi^{n}\pi$ transitions, mixed with some $^{1}\text{LLCT}$/MLCT characters and minor $^{1}\text{LCT}$ signature. In addition, Ir-3 possesses a shoulder at ca. 350 nm that mainly arises from the overlap of the $^{3}\pi^{n}\pi$ state and the $^{1}\text{LLCT}$/MLCT transitions associated with the Nl component, and mixed with some $^{1}\text{LLCT}$/MLCT characters. The emission of Ir-1 – Ir-3 in CH$_{2}$Cl$_{2}$ emanates from the C$^{N}$ ligand-localized $^{3}\pi^{n}\pi$ state based on the TDDFT calculations and the minor solvatochromic effect. These emitting excited states also give rise to broadband triplet excited-state absorption in the visible to near-IR region ($\lambda$). Our studies reveal that extending the $^{1}\text{LLCT}$ state to the lowest-energy $^{1}\text{MLCT}$/LLCT state, followed by a rising time within 150 ps, likely attributed to the decay of the $^{1}\text{MLCT}$/LLCT state (including intersystem crossing to the $^{3}\pi^{n}\pi$ state) after excitation. For Ir-3, the decay of the $^{1}\text{MLCT}$/LLCT state completes within 2 ps. The stronger excited-state absorption of these complexes compared to the ground-state absorption in the visible spectral range leads to strong reverse saturable absorption (RSA) at 532 nm for ns laser pulses and the trend of transmission signal decrease follows Ir-2 > Ir-3 > Ir-1, which correlates well to the combined parameters of the ratio of the ratio of the combined parameters of the ratio of the state (s$_{\sigma}$/s$_{\pi}$) and the triplet excited-state quantum yield ($\Phi_{T}$). Our studies reveal that extending the $\pi$-conjugation of the N$^{N}$ ligand can increase the strength of RSA slightly. In addition, in comparison to the respective Ir(III) complexes with benzothiazolyl substituent on the C$^{N}$ ligand, the naphthalimidyl substitution on the C$^{N}$ ligand dramatically increases the triplet excited-state lifetimes and broadens the triplet excited-state absorption to the NIR region, which could make Ir-1 – Ir-3 broadband reverse saturable absorbers.

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Notes and references

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Electronic Supplementary Information (ESI) available: The optimized geometries of Ir-1 – Ir-3 in CH$_{2}$Cl$_{2}$ via DFT calculations, the $^{1}$H-NMR spectra of Ir-1 – Ir-3 in CDCl$_{3}$, the comparison of the experimental and calculated UV-vis absorption spectra of Ir-1 – Ir-3 and ligand 6 in CH$_{2}$Cl$_{2}$, the absorption spectra and emission spectra of Ir-1 – Ir-3 and ligand 6 in different solvents, the concentration dependent emission spectra and the time-resolved nanosecond transient absorption spectra of Ir-1 – Ir-3 and ligand 6 in CH$_{2}$Cl$_{2}$, the time-resolved fs TA spectra and kinetics of Ir-2 and Ir-3 and ligand 6 in CH$_{2}$Cl$_{2}$, the emission parameters of Ir-1 – Ir-3 and ligand 6 in different solvents, the additional NTOs for the UV-vis absorption of ligand 6, and NTOs contributing to the fluorescence transition from the lowest singlet excited state to the singlet ground state for ligand 6. See DOI: 10.1039/b000000c/

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Table of Content Synopsis

Three cationic Ir(III) complexes with cyclometalating 2-[3-(7-naphthalimidylfluoren-2'-yl)phenyl]pyridine ligands were synthesized and their photophysics and reverse saturable absorption were systematically investigated.