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Author: Mostofa Ataur Rohman Dipankar Sutradhar S. Sangilipandi K. Mohan Rao Asit K. Chandra Sivaprasad Mitra

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Photophysical behavior of systematically substituted (di-2pyridylaminomethyl) benzene ligands and its Re(l) complexes: A combined experimental and theoretical approach

Mostofa Ataur Rohman, Dipankar Sutradhar, S. Sangilipandi, K. Mohan Rao, Asit K. Chandra, Sivaprasad Mitra^{*}

Centre for Advanced Studies, Department of Chemistry, North-Eastern Hill University, Shillong – 793022, India

*To whom correspondence should be addressed. Phone: (91)-364-2722634. Fax: (91)-364-2550076. E-mail: <u>smitranehu@gmail.com</u>, <u>smitra@nehu.ac.in</u>

Abstract

The photophysical behavior of a series of flexible di-2-pyridylaminomethyl substituted ligands systematically substituted on a rigid benzene core and their corresponding mono-metallic Re (I) complexes have been investigated by steady state and time-resolved fluorescence spectroscopy in different composition of DMSO-water binary solvent mixtures. Unusual fluorescence properties in lower DMSO content ($X_{DMSO} = 0.1 \sim 0.3$) solvent mixtures is consistent with fascinating property of DMSO, which is known to perturb the hydrogen bonding ability of water with the solute. Spin allowed inter-ligand $\pi\pi^*$ transition is more apparent in (1, 3) substituted systems. The calculated spectroscopic parameters of the complexes are significantly different from the ligands, mainly due to ligand to metal charge transfer. The experimental observations are in very good agreement with the theoretical results obtained at B3LYP/6-31G(d,p)/LANL2DZ level of density functional theory (DFT) calculation. Natural bond orbital (NBO) analysis and examination of frontier molecular orbitals reveal that the basic architecture of the symmetrically substituted multi-chromophoric ligand can induce excitation energy hopping, similar to an artificial antenna system.

Key-words: (2-pyridyl-aminomethyl) benzene Re(I) complex; time-resolved fluorescence; DFT calculation; energy transfer and trapping; antenna system.

1. Introduction

Controlled synthesis and characterization of three dimensional molecular architectures with suitable core and peripheral subunits are of tremendous interest in the fields of guest-host chemistry, analytical chemistry, optoelectronics, catalysis, biology, and medicine etc. In contrast to the other macromolecules, the size, shape, and functionality of the giant dendritic structures can be defined at the molecular level. The photophysical and functional behavior of the core and peripheral ligands are often suitably chosen to fabricate target designed molecular systems [1-3].

Further, the photophysical and photochemical properties of diamine complexes with d⁶ transition metal (TM) ions, such as rhenium (I), ruthenium (II) and osmium (II) have drawn considerable attention due to their versatile applications in basic science and industry [4]. In general, the advantages of TM-complexes are due to their specific photophysical properties. Due to the presence of strong spin-orbit coupling through the coordinating metal [5, 6], TMcomplexes with suitable organic ligands often show intense phosphorescence at ambient temperature [7 - 9], leading to their applications in organic light emitting diodes (OLEDs) [10] or in other fields such as solar energy conversion, catalysis, as well as medical chemistry [11 -14]. Typically, the excited state decay lifetimes vary within the range of tens of microseconds to several hundred nanoseconds. This is about a few orders of magnitude longer than the typical nanosecond fluorescence lifetime of organic ligands and many orders of magnitude shorter than the corresponding phosphorescence lifetime (milliseconds to seconds) [15]. The situation is particularly suitable for using the signal output from a TM-based probe in biological staining application [16 – 17]. Re (I) tricarbonyl diimine complexes of the type $Re(CO)_3(N^N)L$, where N^N is an aromatic diimine and L is a monodentate ancillary ligand, often show intense and long-lived luminescence typically in the green to orange spectral region. In most cases, the

emission has been assigned to the lowest triplet state of a metal-to-ligand charge transfer (³MLCT) character resulting from a d(Re) $\rightarrow \pi^*$ (diimine) electronic transition [18 – 22]. The photophysical and photochemical properties of the Re(I) tricarbonyl complexes can be tuned by varying their ligand structures. Di-2-pyridylamine is a planar bidentate ligand with powerful binding abilities towards Re (I) metal ion and it can be easily modified by the introduction of substituent groups at its different positions. Also, the introduction of substituent groups such as electron withdrawing or -donating moieties is helpful to tune the energy levels of the novel 2,2'-bipyridine ligand [23 – 24].

In this paper, we report the photophysical behavior of a series of bis, tris, tetrakis-(di-2pyridylaminomethyl)benzene ligands (L1 - L5) and their mononuclear Re(I) complexes (C1 - L5)C5) (structures given in chart 1) studied by steady state and time-resolved fluorescence spectroscopy in conjunction with density functional theory (DFT) calculation. As the solubility of all the compounds is relatively poor in aqueous medium, the basic photophysical studies were done in DMSO solution as well as in a series of DMSO-water mixtures by stepwise addition of water (upto 98% v/v corresponding to X_{water} = 0.99) for all the systems. It is to be noted here that the possibility of any aggregate formation in the higher water content solution mixture is eliminated by dynamic light scattering (DLS) experiment as well as transmission electron microscope (TEM) measurement. A series of different spectroscopic experiments are already reported to reveal the exceptional behavior of DMSO-water mixed solvent system [25 - 27]. Also, the mixture of DMSO and water is known to have extensive biological importance [28 -32]. The physico-chemical properties of these mixtures deviate strongly from the continuum behavior and differ to a large extent from that expected in the additive rule [33]. Therefore, to understand the fluorescence behavior of systematically substituted di-2-pyridylaminomethyl-

benzene ligands and the corresponding Re (I) complexes seems to be interesting from a fundamental point of view, particularly in the mixture with varying DMSO-water composition.

2. Experimental details

2.1. Materials

2.1.1. Ligands: Synthesis and characterization of the ligands (L1 - L5) were done according to literature reports published elsewhere [34, 35]. In this section, we present the results in brief.

1,2-Bis(di-2-pyridylaminomethyl)benzene (L1). Di-2 pyridylamine (1.00 g, 5.84 mmol) and potassium hydroxide (1.33 g, 23.7 mmol) were stirred in DMSO (5 mL) for 1 h; 1,2 bis (bromomethyl)benzene (0.70 g, 2.65 mmol) was added and the reaction mixture was stirred for a further 40 h. Water was then added until the solution turned cloudy. The yellow precipitate that formed was isolated and recrystallized from an ethyl acetate– petroleum ether (bp 30–60 °C) solution to yield yellow crystals. Yield, 0.29 g (25%); mp 144–146 °C. Found: C, 75.37; H, 5.38; N, 19.04. Calc. for $C_{28}H_{24}N_6$: C, 75.65; H, 5.44; N, 18.91%. 1H NMR (500 MHz, CDCl₃, 296 K) d 8.32 (4H, d, py), 7.53 (4H, t, py), 7.27 (2H, d, ph), 7.22 (4H, d, py), 7.04 (2H, t, ph), 6.86 (4H, dd, py), 5.64 (4H, s, CH₂). ¹³C NMR (125.76 MHz, CDCl₃, 296 K) d 157.1 (C5), 148.2 (C1), 137.2 (C7), 136.1 (C3), 126.5, 126.4 (C8, C9), 117.2 (C2), 114.6 (C4), 48.6 (C6). MS (HR-ESI): m/z 444.2079; $C_{28}H_{24}N_6$ requires 444.2063.

1,3-Bis(di-2-pyridylaminomethyl)benzene (L2). Di-2pyridylamine (1.00 g, 5.84 mmol) and potassium hydroxide (1.33 g, 23.7 mmol) were stirred in DMF (30 mL) at 40 °C for 20 min. 1,3-bis (bromomethyl)benzene (0.699 g, 2.65 mmol) was added and stirring was continued at 40 °C for a further 40 h. The solvent was removed under reduced pressure and the residue partitioned between dichloromethane (200 mL) and water (150 mL). The organic layer was washed twice with water (2×150 mL) and then the combined aqueous phases washed with dichloromethane (2

× 100 mL). The combined dichloromethane layers were dried (Na₂SO₄) and then evaporated, resulting in a pale yellow solid. This was recrystallized from acetone–water yielding 980 mg (83%) of a yellow crystalline solid; mp 133–134 °C. Found: C, 75.46; H, 5.49; N, 19.03. Calc. for $C_{28}H_{24}N_6$: C, 75.65; H, 5.44; N, 18.91%. 1H NMR (500 MHz, CDCl₃, 296 K) d 8.25 (4H, d, py), 7.53 (4H, t, py), 7.27 (2H, d, ph), 7.22 (4H, d, py), 7.04 (2H, t, py), 6.86 (4H, t, py), 5.64 (4H, s, CH₂). ¹³C NMR (500 MHz, CDCl₃, 296 K) d 157.0 (C5), 148.1 (C1), 139.3 (C7), 137.1 (C3), 128.4 (C9), 125.3 (C10), 125.1 (C8), 117.2 (C2), 114.5 (C4), 51.20 (C6).

1,4-Bis(di-2-pyridylaminomethyl)benzene (L3). Di-2-pyridylamine (1.00 g, 5.84 mmol) and potassium hydroxide (1.33 g, 23.7 mmol) were stirred in DMF (30 mL) at 40 °C for 20 min.1,3-Bis(bromomethyl)benzene (0.699 g, 2.65 mmol) was added and stirring was continued at 40 °C for a further 40 h. The solvent was removed under reduced pressure and the residue partitioned between dichloromethane (200 mL) and water (150 mL). The organic layer was washed twice with water (2 × 150 mL) and then the combined aqueous phases washed with dichloromethane (2 × 100 mL). The combined dichloromethane layers were dried (Na₂SO₄) and then evaporated, resulting in a pale yellow solid. This was recrystallized from acetone–water yielding 780 mg (66%) as a yellow powder; mp 181–183 °C. Found: C, 75.47; H, 5.44; N, 19.01. Calc. for C₂₈H₂₄N₆: C, 75.65; H, 5.44; N, 18.91%. 1HNMR (500 MHz, CDCl₃, 296 K) d 8.28 (4H, d, py), 7.47 (4H, t, py), 7.22 (4H, s, ph), 7.13 (4H, d, py), 6.82 (4H, dd, py), 5.43 (4H, s, CH₂). ¹³C NMR (500 MHz, CDCl₃, 296 K) d 157.1, 148.1, 137.6, 137.1, 126.9, 117.1, 114.5, 51.02. MS (HR-ESI): m/z 444.2078; C₂₈H₂₄N₆ requires 444.2063.

1,3,5-Tris(di-2-pyridylaminomethyl)benzene (L4). This was prepared by an adaptation of a published procedure.7 Di-2- pyridylamine (1.00 g, 5.84 mmol) and potassium hydroxide (1.31 g, 23.4 mmol) were stirred in DMSO (5 mL) for 1 h. 1,3,5- Tris(bromomethyl)benzene19 (0.675

g, 1.89 mmol) was then added and the solution stirred for an additional 48 h. Water was added dropwise until the solution turned cloudy. On standing, a yellow precipitate formed which was filtered off, washed with water and recrystallized from an ethyl acetate–petroleum ether (bp 30–60 °C) mixture. Yield, 0.583 g (49%); mp 158–160 °C. Found: C, 74.33; H, 5.07; N, 19.80. Calc. for $C_{39}H_{33}N_9$: C, 74.62; H, 5.30; N, 20.08%. 1H NMR (500 MHz, CDCl₃, 296 K) d 8.20 (6H, d, py), 7.37 (6H, t, py), 7.07 (3H, s, ph), 6.91 (6H, d, py), 6.78 (6H, dd, py), 5.34 (6H, s, CH₂). ¹³C NMR (125.76 MHz, CDCl₃, 296 K) d 157.0, 148.0, 139.4, 137.0, 123.6, 116.9, 114.5, 51.18. MS (HR-ESI): m/z 628.2937. $C_{39}H_{34}N_9^+$ requires 628.2953.

1,2,4,5-Tetrakis(di-2-pyridylaminomethyl)benzene (L5). Di-2-pyridylamine (1.00 g, 5.84 mmol) and potassium hydroxide (1.31 g, 23.4 mmol) were stirred in DMSO for 1 h, 1,2,4,5-tetrakis(bromomethyl)benzene (0.642 g, 1.89 mmol) was added and the solution stirred for a further 48 h. Addition of water gave a yellow precipitate which was washed with water and then recrystallized from a chloroform–petroleum ether mixture. Yield: 0.396 g (34%); m.p. 238–241 $^{\circ}$ C. Calc. for C₅₀H₄₂N₁₂ .2H₂O: C, 70.90; H, 5.47; N, 19.84. Found: C, 71.03; H, 5.36; N, 20.01%. ES-MS m/z = 811 [M+H]⁺. HRMS: calc. for [C₅₀H₄₃N₁₂]⁺ 811.3729; found 811.3734. 1H NMR (CDCl₃): d 8.16 (d, 8H, H1), 7.33 (Br, 8H, H3), 7.14 (s, 2H, H8), 6.84 (d, 8H, H4), 6.78 (dd, 8H, H2), 5.42 (s, 8H, H6). 13C NMR (CDCl₃): d 156.8 (C5), 148.0 (C1), 137.0 (C3), 133.6 (C7), 123.6 (C8), 116.9 (C2), 114.5 (C4), 52.1(C6).

2.1.2. Re(I) complexes (CI - C5) of the ligands: The general procedure [36] of the synthesis of Re(I) complexes can be described as follows. A mixture of [Re(CO)₅Br] (50 mg, 0.123 mmol) and the corresponding 2,2'-dipyridylamine ligands (L1-L5) (0.123 mmol) were taken in 1:1 M ratio in a two neck Schlenk flask fitted with a reflux condenser. The whole system was evacuated to 2-3 times, nitrogen was purged and 20 ml of freshly distilled toluene was added by using

syringe in the nitrogen atmosphere. The respective reaction mixture was stirred and heated up to 60-70 °C for 5-12 h and then allowed to cool to room temperature. Solvent was removed by rotatory evaporator and the solid mixture was washed with hexane to remove the unreacted starting precursor and the crude product was further purified by column chromatography in neutral alumina by using hexane/ethyl acetate mixture in 1:2 ratio as an eluent to give pale yellow or yellow products.

[**Re**(**CO**)₃(**1,2-bis-DPA**)**Br**] (**C1**). Yield: 38 mg (76%); IR (KBr): v 2020 (vs), 1909 (vs), 1892 (vs), 1601 (w), 1583 (w), 1468 (m), 1437 (w), 1425 (w), 1239 (w), 771 (w), 756 (w) cm⁻¹; 1H NMR (400 MHz, CDCl₃, 25 °C): d 8.98 (d, 2H, J ¼ 1.2 Hz, CH(py)), 8.91 (t, 4H, CH(py)), 8.30 (d, 2H, J ¼ 4 Hz, CH(py)), 7.72 (t, 4H, CH(py)), 7.19 (s, 4H, CH(benzyl)), 7.13 (d, 4H, J ¼ 6.4 Hz, CH(py)), 5.24 (s, 4H, CH₂) ppm; ESI-MS (m/z): 796.68 [M⁺]; UV-Vis {Acetonitrile, λ_{max} , nm (ϵ /10⁴ M⁻¹ cm⁻¹)}: 261 (0.95), 298 (1.02); Anal. Calc. for C₃₁H₂₄N₆O₃BrRe (794.67): C, 46.85; H, 3.04; N, 10.58. Found: C, 46.92; H, 3.33; N, 10.69%.

[**Re**(**CO**)₃(**1**,**3**-**bis**-**DPA**)**Br**] (**C2**). Yield: 32 mg (64%); IR (KBr): v 2020 (vs), 1908 (vs), 1884 (vs), 1601 (w), 1583 (w), 1468 (m), 1438 (w), 1376 (w), 1111 (w), 774 (w), 754 (w) cm⁻¹; 1H NMR (400 MHz, CDCl₃, 25 °C): d 8.95 (d, 4H, J ¹/₄ 5.6 Hz, CH(py)), 7.79 (s, 1H, CH(benzyl)), 7.69 (t, 4H, CH(py)), 7.40 (d, 2H, J ¹/₄ 7.6 Hz, CH(benzyl)), 7.29 (t, 1H CH(benzyl)), 7.16 (d, 4H, J ¹/₄ 8.0 Hz, CH(py)), 7.07 (t, 4H, CH(py)), 5.03 (s, 4H, CH₂) ppm; ESI-MS (m/z): 797.21 [M⁺]; UV-Vis {Acetonitrile, λ_{max} , nm (ε/10⁴ M⁻¹ cm⁻¹)}: 210 (2.00), 254 (1.24), 298 (1.41); Anal. Calc. for C₃₁H₂₄N₆O₃BrRe (794.67): C, 46.85; H, 3.04; N, 10.58. Found: C, 46.69; H, 3.23; N, 10.83%.

[**Re**(**CO**)₃(**1,4-bis-DPA**)**Br**] (**C3**). Yield: 40 mg (80%); IR (KBr): v 2021 (vs), 1909 (vs), 1892 (vs), 1601 (w), 1583 (w), 1467 (m), 1439 (w), 1424 (w), 1111 (w), 774 (w), 756 (w) cm⁻¹; 1H

NMR (400 MHz, CDCl₃, 25 °C): d 8.92 (d, 2H, J ¹/₄ 4.4 Hz, CH(py)), 8.25 (d, 2H, J ¹/₄ 3.6 Hz, CH(py)), 8.21 (d, 4H, J ¹/₄ 4.0 Hz, CH(py)), 7.14 (d, 4H, J ¹/₄ 5.6 Hz, CH(benzyl)), 7.44 (t, 4H, CH(py)), 6.76 (t, 4H, CH(py)), 5.35 (s, 4H, CH₂) ppm; ESI-MS (m/z): 796.43 [M⁺]; UV-Vis {Acetonitrile, λ_{max} , nm ($\epsilon/10^4$ M⁻¹ cm⁻¹)}: 226 (0.49), 252 (0.33), 297 (0.34); Anal. Calc. for C₃₁H₂₄N₆O₃BrRe (794.67): C, 46.85; H, 3.04; N, 10.58. Found: C, 47.02; H, 3.37; N, 10.79%.

[**Re**(**CO**)₃(**1**,**3**,**5**-**tris-DPA**)**Br**] (**C4**). Yield: 41 mg (82%); IR (KBr): v 2018 (vs), 1909 (vs),1889 (vs), 1597 (w), 1583 (w), 1467 (m), 1424 (m), 1375 (w), 1230 (w), 712 (w), 754 (w) cm⁻¹; 1H NMR (400 MHz, CDCl₃, 25 °C): d 8.87 (d, 2H, J ¼ 4.0 Hz, CH(py)), 8.13 (t, 6H, CH(py)), 7.07 (s, 3H, CH(benzyl)), 6.90 (d, 4H, J ¼ 8.0 Hz, CH(py)), 6.85 (d, 6H, J ¼ 8.0 Hz, CH(py)), 6.73 (t, 6H, CH(py)), 5.34 (s, 6H, CH₂) ppm; ESI-MS (m/z): 978.05 [M⁺];UV-Vis {Acetonitrile, λ_{max} , nm ($\epsilon/10^4$ M⁻¹ cm⁻¹)}:: 227 (0.57), 275 (0.39), 299 (0.46); Anal. Calc. for C₄₂H₃₃N₉O₃BrRe (977.88): C, 51.59; H, 3.40; N, 12.89. Found: C, 51.81; H, 3.57; N, 13.03%.

Re(**CO**)₃(1,2,4,5-tetrakis-**DPA**)**Br**] (C5). Yield: 35 mg (70%); IR (KBr): v 3423 (w), 2019 (s), 1907 (s), 1892 (s), 1599 (w), 1584 (w), 1468 (m), 1425 (m), 1377 (w), 1237 (w), 1152 (w), 772 (w) cm⁻¹; 1H NMR (400 MHz, CDCl₃, 25 °C): d 8.31 (d, 2H, J ¼ 3.6 Hz, CH(py)), 8.20 (d, 6H, J ¼ 7.2 Hz, CH(py)), 7.51-7.49 (m, 8H, CH(py)), 7.29 (s, 2H, CH(benzyl)), 6.89-6.71 (m, 16H, CH(py)), 5.50 (s, 8H, CH₂) ppm; ESI-MS (m/z): 1183.88 [M+Na]⁺; UV-Vis {Acetonitrile λ_{max} , nm ($\epsilon/10^4$ M⁻¹ cm⁻¹)}: 228 (0.98), 298 (0.85), 387 (0.06); Anal. Calc. for C₅₃H₄₂N₁₂O₃BrRe (1161.09): C, 54.82; H, 3.65; N, 14.48. Found: C, 55.07; H, 3.59; N, 14.83%.

2.2. Instruments and data analysis

Steady-state absorption and corrected fluorescence spectra were recorded on Perkin-Elmer (model Lambda25) absorption spectrophotometer and Hitachi (model FL4500) spectrofluorimeter, respectively. The final concentration of chromophores was adjusted at ca. 10

 μ M in the solutions used for spectral measurement. In fluorescence emission and excitation spectra measurements, 5/5 nm band pass was used in both the excitation and emission sides. Fluorescence quantum yields (\Box_f) were calculated by comparing the total fluorescence intensity (F) under the whole fluorescence spectral range with that of quinine bisulfate in 0.5M H₂SO₄ ($\Box_f^S = 0.546$) [37, 38] by using Eq. (1).

$$\phi_f^i = \phi_f^s \cdot \frac{F^i}{F^s} \cdot \frac{1 - 10^{-A^s}}{1 - 10^{-A^i}} \cdot (\frac{n^i}{n^s})^2 \tag{1}$$

Where, A_i and A_s are the optical density of the sample and standard, respectively, and n_i is the refractive index of solvent at 298 K. The relative experimental error of the measured quantum yield was estimated within $\pm 10\%$.

The fluorescence decay curves were obtained by using 295 nm LED excitation in a Pico Master time correlated single photon counting (TCSPC) lifetime apparatus (PM-3) supplied by Photon Technology International Inc. (PTI). The instrument response function (IRF) was obtained by using a dilute colloidal suspension of dried non-dairy coffee whitener. The experimentally obtained fluorescence decay traces I(t), collected at the magic angle (54.7⁰) to eliminate any contribution from the anisotropy decay, were expressed as a sum of exponentials (Eq. 2) and analyzed by non–linear least–square iterative convolution method based on Lavenberg–Marquardt algorithm [39] as implemented in the data analysis software (Felix GX version 4.0.3) from PTI

$$I(t) = \sum_{i} \alpha_{i} \exp(\frac{-t}{\tau_{i}})$$
⁽²⁾

Where, α_i is the amplitude of the ith component associated with fluorescence lifetime τ_i such that $\Box \alpha_i = 100$. The reliability of fitting was checked by numerical value of reduced chi- square (χ^2), Durbin–Watson (DW) parameter and also by visual inspection of residual distribution in the

whole fitting range. All experiments were carried out at ambient temperature of 298 K, and the other spectral parameters like average fluorescence lifetime ($\langle \tau \rangle$), radiative and total non-radiative rate constants (k^r and Σ k^{nr}, respectively) were calculated by using equations (3), (4) and (5), respectively.

$$<\tau> = \frac{\sum_{i} \alpha_{i} \tau_{i}^{2}}{\sum_{i} \alpha_{i} \tau_{i}}$$
(3)
$$k^{r} = \frac{\Phi_{f}}{<\tau>}$$
(4)
$$\sum_{i} k^{nr} = \frac{1 - \phi_{f}}{<\tau>}$$
(5)

2.3. Density functional theory (DFT) calculation.

The geometries of the ligands (L1-L5) and their corresponding Re(I) complexes (C1-C5) were optimized using DFT based B3LYP method [40] in conjugation with 6-31G(d,p) basis set for the lighter atoms (C, H, N and O) and LANL2DZ basis set for the heavier atoms (Re and Br). The 6-31G(d,p) is a standard polarized basis set, which adds d function on heavier atoms and p function on lighter atoms; whereas, LANL2DZ is a pseudo potential basis set frequently used for post third row atoms [41, 42]. Harmonic frequency calculations were carried out at the same level to characterize the stationary points to ensure that the optimized geometries are minima on the potential energy surface (PES). The Time dependent-DFT (TD-DFT) method [43] was used to calculate the electronic absorption spectra of the complexes. In order to incorporate the effect of the solvent around the molecule, the Polarizable Continuum Model (PCM) [44] was employed in TD-DFT calculations. The percentage composition of the molecular orbital analysis was carried out by Chemissian software package [45]. All the electronic structure calculations were carried out using Gaussian09 suite of program [46].

3. Results and Discussion

3.1. Steady state spectra of ligands and Re (I) complexes.

Representative electronic absorption spectra of ligands and it's Re(I) complexes are illustrated in figure 1; while the corresponding plots for all the systems are given in figure S1 in supplementary section. The main intense absorption band ($\epsilon \sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) of the ligands is around 300 nm in DMSO and shifts to 304 – 309 nm range in 98% (v/v) water (X_{water} =0.99). Also, in the case of multi-chromophoric structures like trimer and tetramer, a lower energy broad peak is introduced around 375 - 394 nm due to the spin allowed intramolecular inter ligand $\pi\pi^*$ transition. With increasing mole fraction of water, vibrational structure in this absorption band becomes prominent (Figure S1). The absorption behavior of the complexes is almost similar to the respective ligands. The main intense band again appears at around 300 nm. However, in case of Re(I) complexes, the structural features as well as intensity of the low energy absorption band is relatively less in comparison with the ligands, due to ligand to metal charge transfer as confirmed by theoretical calculation result discussed later.

All the ligands give emission at around 360 nm when excited at 300 nm absorption in pure DMSO. However, on further increasing the mole fraction of water, the emission peak gets shifted towards 410 nm with substantial broadening in spectral width (figure 2a). These results indicate that increasing the water content in the solvent mixture produces a new "solvent relaxed" emissive state which is stabilized by ca. 3250 cm⁻¹ than the corresponding Frank-Condon excited state in pure DMSO. Interestingly, in the mixtures containing very low DMSO content, the stabilization of the excited state is not apparent; in fact, the emissive state becomes less stable by ca. 1000 cm⁻¹ for L1. Similar observation is also observed for other ligands, but to a different extent. This observation, although seems to be contradictory in nature, can be

explained by the recent studies of Bagchi et. al. [47] and subsequent experimental findings by Sarkar et. al. in different systems [48, 49]. Based on simulation studies, Bagchi and coworkers have proposed that at low mole fraction of DMSO, an abrupt increase in the hydrophobicity of the DMSO–water mixture occurs, which destabilizes polar solute to a greater extent. Therefore, the shift in fluorescence spectral peak position in high water content solution is considered to be due to the stabilization of polar excited state in the solvent cage of water. Stabilization of the polar excited state resulting highly solvent dependent luminescence from Ru(II) complexes is already reported in the literature [50]. The polar nature of the emissive state in the present systems is further confirmed by critically reviewing the spectral shift (inset of figure 2a). For example, the destabilization at the region characterized by $X_{DMSO} < 0.1$ is only 250 cm⁻¹ for L3 in contrast to ca. 1000 cm⁻¹ of the corresponding parameter for L1. This observation is consistent with the polarity of the ligands (L3 is least polar among the bi-chromophoric compounds; whereas, the polarity of L1 is expected to be highest) and corroborates nicely with the DFT calculation results (see below).

Furthermore, in case of higher order ligands like trimer (L4) and tetramer (L5), the emission intensity is very weak (see below for a comparison on relative fluorescence yield for different ligands and figure S1) and the spectral profile consists of two distinctly visible peaks; one corresponds to the 360 nm as observed in L1 – L3 and the other very broad peak within 400~550 nm region, particularly at higher water content solution. Interestingly, this broad emission peak shows striking resemblance with the emission spectrum obtained by exciting the sample at low energy absorption band (ca. 375 nm) as shown in the inset of figure 2b. Therefore, the long wavelength absorption (375 ~ 394 nm) and the corresponding broad emission (400 ~ 550 nm) can be assigned to a new emitting state or species, which is more facile to form in case

of multi-chromophoric systems with excess water content in solvent mixture. A possible explanation on the origin of these spectral features can be drawn from the conformational analysis of the ligands. A significant steric repulsion between the adjacent pyridylaminomethyl units is expected in L1 and/or L5 leading to a twisted conformation in contrast to L2, L3 and L4, where the chromophoric sub-units are well separated. However, as the low-energy absorption and/or emission bands are observed only in case of higher order ligands, the importance of twisting in the photophysical behavior can be ruled out. Rather, the spin allowed intramolecular inter-ligand type of interaction, hypothesized earlier, becomes more pertinent in higher order systems studied here, particularly in high water content (less viscous) solvent mixtures due to greater flexibility of the branched chromophores.

The general trend of fluorescence for mono-metallic Re (I) complexes (C1 – C5) in different DMSO-water mixtures are similar to that observed for the corresponding ligands (L1 – L5). A representative plot for C4 is shown in figure 2b. The only notable difference is significantly less fluorescence spectral shift observed in case of the complexes relative to their ligand counterpart (figure S1). For example, the fluorescence peak shifts from 360 nm in pure DMSO to 393 nm only ($\Delta E = ~2330 \text{ cm}^{-1}$) in 40% (v/v) DMSO-water mixture in case of C1. Therefore, the emissive states of the metal complexes are considered to be significantly less polar in comparison with the ligands. DFT calculation results for the dipole moment of the investigated systems (see below) indeed confirm this prediction.

The emission properties of all the ligands and the complexes were checked with varying excitation wavelength within the whole absorption profile. Representative plots for all the systems are shown in supplementary section (figure S2). Except certain changes in the intensity, the emission spectral profile remains invariant in all the cases suggesting that the primary

photophysical behavior is mostly due to the ligands only, even in case of the metal complexes. Earlier report on the non-luminescent Re complexes of several di(2-pyridyl)amine based ligands was ascribed mainly due to the metal centered excited state or phosphorescence from ³MLCT state [51]. However, almost similar spectral behavior of the metal complexes with their corresponding ligand counterpart observed in the present study emphasizes mainly ligand centered absorption (even in presence of metal). This is probably due to very weak molar absorption coefficient of the MLCT state in comparison with very strong $\pi^* \leftarrow \pi$ ligand absorption.

3.2. Quantum yield of fluorescence of the ligands and Re(I) complexes.

Fluorescence quantum yields (ϕ_t) of all the systems were measured in different solvent mixtures with varying water content. The representative spectral data of all the investigated systems in some selected solvent systems are collected in table 1; while, the detailed result of the individual systems in different solvent mixtures are given in supplementary section (table 1S and 2S). In general, ϕ_t of the ligands are at least one order of magnitude higher than that of the corresponding complexes, which further emphasize on the $d\pi(\text{Re})-\pi^*$ type (see DFT calculation results also) metal to ligand transition in the complexes. It is further to be noted that ϕ_t of L3 is highest among all the ligands; while the same is true for C3 among all the complexes. It is found to be the lowest in the cases L2 (or C2) and L5 (or C5). These observations are consistent with the assumption of inter-ligand cross talk between the neighboring di-2-pyridylaminomethyl groups in the multi-chomophoric systems mentioned above. Similar observations were also noted in the cases of polyphenylene dendrimers with multiple peryleneimide chromophores in the rim [52]. The intramolecular energy hopping in the multi-chromophoric dendritic structures were shown to occur via Förster mechanism within

ultrafast time scale of 100~200 ps [53]. The efficiency of energy transfer depends critically on the spatial arrangement of interacting chromophores, i.e. the geometric distribution between the transition dipole moments and also the distance between the donor and acceptor pair, the so called critical Förster distance, R_0 [54]. The exact nature of the transition dipole moment distribution between the donor-acceptor pair is unknown at this point for any of the investigated systems. Therefore, quantitative comparison of the excitation energy transfer efficiency among different systems is not possible. However, a qualitative description for the observed difference in fluorescence yield can be put forward by comparing the inter-chromophoric distances in different ligands with an assumption of random dipole moment distribution. The distance between two amino-methyl-pyridyl chromophores in L1, L2 and L3 are 3.42, 4.95 and 7.53 Å, respectively [34]. Among these, the efficiency of energy transfer is highest in L2 (lowest ϕ_f); therefore, the critical distance (R_0) for efficient energy transfer can be assumed to be ca. 5.0 Å. The para substituted ligand (L3) can be considered as a model system, where inter-chromophoric interaction is the lowest; therefore showing highest ϕ_f among the lot. On the other hand, the distance between the two chomophores in L1 seems to be too short ($R << R_0$), so the efficiency of energy transfer is very less. This may explain the observed ϕ_f in the case of L1, which is quite close to L3 (figure 3a). Interestingly, the ϕ_f value in case of L4 is quite close to L2. From the Xray crystal structure data [34], it is apparent that although this system contains three 1,3 substituted chromophores, only one pair of them are in the range of R_0 (R = 4.9Å); the other two distances (6.7 and 7.4 Å, respectively) are very large and therefore are not expected to contribute in the energy transfer process significantly.

Further, the variation in ϕ_f with solvent composition shows some peculiar behavior. With increasing water content in solution, the quantum yield of both the ligands as well as complexes

increases initially. This is consistent with the stabilization of relatively more polar emitting state with increasing polarity of the solvent. However, the magnitude of ϕ_f increases only upto certain mole fraction of water, typically $X_w \sim 0.7$ for ligands and 0.8 in case of the complexes (figure 3). It is well known from the earlier studies that at low DMSO (or higher water) content, the solution mixture forms several hydrogen bonded water-DMSO complexes [47, 48], and therefore, the local water structure near the probe becomes more hydrophobic in nature and cannot stabilize the polar emissive species.

3.3. Time resolved fluorescence studies on the ligands and Re(I) complexes.

Time resolved fluorescence decay behavior of all the ligand and complexes were measured by monitoring the fluorescence at their respective emission wavelength in several DMSO-water mixtures. At least two exponential decay model in Eq. 2 was necessary to fit all the data with acceptable statistical parameters as evidenced by some representative fluorescence decay fittings of **L5** and **C3** shown in figure 4. While τ_{av} , the average fluorescence decay time (calculated using Eq. 3), of individual systems are listed in table 1, the results of complete decay analysis of all the systems are shown in supplementary section (tables 3S and 4S). In general, the magnitude of τ_{av} for the metal complexes are higher than the corresponding ligands. The calculated values of radiative (k^r) and sum of total non-radiative (Σk^{nr}) rate constants for different systems are also shown in table 1.

Time-resolved fluorescence decay shows interesting modulation with solvent composition for all of the investigated systems. Representative examples are shown in figure 5 for L3 (para substituted dimer) and L4 (1,3,5 substituted trimer). The correosponding plot for the other systems are shown in the supplementary section (figure S3). It is clear that the decay pattern changes completely with varying water content in the solution. Furthermore, the trend in

variation of the deacay profile is almost opposite in case of L4 while comparing with L3. To understand more about solvent dependent fluorescence decay behavior of all the investigated systems, global analysis of the fluorescence decay data was performed for individual systems in different solvent mixtures. Two lifetimes related with the fast and slow decay components ranging within $\tau(\text{fast}) = 0.8 \sim 1.7$ ns and $\tau(\text{slow}) = 2.9 \sim 6.8$ ns are observed for the ligands; while the corresponding values for the complexes are found to be within 1.1~2.6 and 5.2~9.4 ns, respectively. To verify the possible involvement of phosphorescence decay associated with long lifetime, particularly in case of Re complexes, all the luminescence measurements were repeated under deoxygenation condition by saturating the solution with argon gas. However, no difference in the luminescence spectral profile as well as in the time resolved decay behavior taken over whole emission spectral range were observed in any of the systems (supplement figure S4). Also, typical phosphorescence lifetime from the ³MLCT state of Ru(II) and Ir(III) complexes are known to be within a few hundreds of picosecond to tens of microsecond time scale [55, 56]. Furthermore, the variation in relative amplitude of the long decay component with solvent composition show similar pattern for both the ligands and the complexes in the present study (see below). Therefore, the decay component ranging within 5.2~9.4 ns in case of metal complexes is considered not to be due to any phosphorescent state; however, the possibility of inter system crossing and thermally activated delayed fluorescence (TADF) can not be ruled out at this point. This is more relevant as some of the recent reports suggested very efficient TADF in metal complexes with intra-ligand charge transfer properties [57, 58]. Interestingly, the relative amplitude associated with the fast decay component, a(fast), is always predominant (>90%) in pure DMSO or in the DMSO-water mixture with 98% (ν/ν) water content. However, interesting modulation in relative population is observed at low DMSO content of the solution

 $(X_{water} = 0.8)$, particularly for the ligands. In all the cases, the contribution from the slow decay component, a(slow), increases considerably (upto 30~40%) under this condition. Some of the representative plots are shown in figure 6. These results indicate that the species associated the faster decay component is considerably polar in nature and therefore, predominates in highly polar media. However, in the solvent with $X_{DMSO} = 0.8$, where the hydrophobic nature of the solvent system becomes important, the relatively non-polar species responsible for the slow decay component also contributes significantly in the fluorescence emission. This observation is also consistent with the fact that fluorescence emission spectrum in almost all the cases show significant broadening in the solution mixture with $X_{water} = 0.8$ (figure 2) discussed above. It is noted here that a complete picture on the solvent modulation of fluoescing species can be obtained by constructing the decay associated spectra fluorescence and there is also components at different wavelengths in the whole emission spectral profile under varying solvent composition.

3.4. DFT calculation results on the ligands and Re(I) complexes.

3.4.1. Optimized Geometries. The geometries of all the metal complexes are found to be closed shell structures and no parameter is kept constrained during their optimization. It should be noted that, in a previous work we have already reported the theoretical studies for the complexes C2, C4 and C5 [36]. In this present work, we report various theoretical results for all the ligands and their corresponding metal complexes to substantiate the experimental results discussed in the previous sections. It has been already observed that the various geometric parameters such as bond lengths (r) and bond or dihedral angles (θ or δ , respectively) for the complexes are in well agreement with the single crystal X-ray structural data which accounts for the reliability of the theoretical method (B3LYP/6-31G(d,p)/LANL2DZ) used for the present work. The distance between two amino-methyl-pyridyl chromophores i.e, distance from one methelene carbon to the

other methelene carbon in L1, L2 and L3 are 3.02, 5.05 and 5.86 Å, respectively which is in good agreement with experimental data described above. The ground state dipole moments for the ligands (L1-L5) computed at the B3LYP/6-31G(d,p) level of theory are found to be 4.74, 4.80, 4.39, 5.60 and 1.62 D, respectively. As expected, among all the bis-complexes, L3 has the lowest dipole moment than the other two ligands. This difference can be accounted for the higher symmetry in the geometry of L3 molecule. Similar effect can be observed for L5 as well. A schematic representation of the ligands is shown in scheme - I. It should be noted that the Re metal coordinates to the ligand through N2 and N3 of fragment A in the complexes C1 - C5. Almost for all the ligands, θ (C1C7N1) is found to be 116° and negligible variation has been observed for the metal complexes. On the other hand, δ (C1C7N1C9) for ligands L1 - L4 ranges between 95°~98°; whereas, for L4, the corresponding value of 62° has been predicted. On complex formation, the same dihedral angle decreases to 88°, 48°, 42° and 41° for C1, C2, C4 and C5; whereas, for C3 it increases to 162°. The induced planarity of the pyridylaminomethyl ligand with the rigid benzene core on complex formation ensures MLCT type of transition mentioned earlier. Interestingly, δ (C1C7N1C10) for L1 - L4 ranges between -78° ~ -83°: whereas for L5, an angle of -139° has been predicted. On complex formation, this angle varies within -150° to -163° for C2, C4 and C5; whereas for C1 and C3, a value of -84° and -37° has been predicted. The bond distance r(N2-N3) in ligands L1-L4 ranges between 3.02~3.05 Å; whereas for L5, a slight higher value of 3.76 Å has been observed. These distances reduce to 2.82, 2.87, 2.92, 2.93 and 2.96 Å, respectively for C1-C5 on complex formation.

The charges on the individual atoms for ligands and the metal complexes obtained from Natural Bond Orbital (NBO) analysis [59] are listed in table 5S. The charges on the Re atom for the metal complexes ranges between -0.9615e and -0.9963 which are lower than the formal

charge of Re i.e. +1. On the other hand, the NBO charges on N1, N2 and N3 atom for L1-L3 are found to be -0.473e, -0.453e and -0.490 e. On complexation, N1, N2 and N3 loses its negative charge partially and attains a value of -0.448, -0.412 and -0.425e; -0.467, -0.422 and -0.423e; and -0.446, -0.410 and -0.416 e for complexes C1, C2 and C3, respectively. A similar decrease in N charges has been observed for C4 and C5 as well, except for a slight increase in N3 charge in complex C5 (as indicated in Table 5S). All these results suggest that there is a charge transfer (CT) from ligand to Re(I) metal (LMCT) on complex formation.

3.4.2. Nature of Frontier Molecular Orbitals. The HOMO-LUMO energy gap is known to be a good measure for the absorption spectral peak position of a molecule. The HOMO-LUMO energy gap (ΔE) for all the ligands are found to range between 4.38 ~ 4.58 eV (corresponding to 283 ~270 nm). On complex formation, the corresponding value calculated for C1-C5 reduces to 3.78, 3.75, 3.67, 3.53 and 3.85 eV, respectively (328 ~ 322 nm). The frontier molecular orbital diagram as well as the composition of molecular orbital analysis of all the ligands suggests that the HOMO (nearly 90%) is mainly located in the pyridylamine moiety (fragment A, scheme I); whereas, LUMO is located on the other pyridylamine moiety (fragment A1 for L1, A2 for L2, A3 for L3 and A_2 for L4). This pattern is consistent for all the ligands except for L5, where about 70% of the HOMO is located on fragment A but a small percentage of HOMO (15% and 16%) is spread over A_5 and A_2 as well (figure S5). It is to be noted that this complete reversal of electron density on excitation from one fragment to the other confirms the possibility of inter-ligand cross talk in the excited state in a particular molecule, hypothesized earlier from the fluorescence spectral data. From the % composition of the molecular orbital analysis for metal complexes, it can be concluded that HOMO (ranging between 40-63 %) is mostly located on the Br atom for complexes C1, C2, C3 and C5; whereas for complex C4, it is located on the ligand itself (figure

S6). Unlike other complexes, almost 30% of the HOMO for C5 is located on the *meta* substituted A_2 fragment. This pattern is missing in other complexes. On the other hand, more than 90% of LUMO is located on fragment A of the ligand for all the complexes.

The electronic absorption spectra were calculated using the TD-DFT method in two different solvents (DMSO and H₂O) employing PCM model, which essentially deals the solvent as a dielectric continuum. The calculated and the experimental absorption data, HOMO-LUMO energy gaps, oscillator strength and the character of electronic transitions are listed in table 2. Some of the representative figures are also in supplementary section (figure S7). In agreement with the experimental results, theoretical calculations also predict an intense absorption band of the ligands (L1-L5) at around 290 nm in DMSO. However, no significant shift in absorption peak is observed in aqueous medium within the PCM framework. Therefore, it can be argued that experimentally observed long wavelength absorption band in aqueous medium (particularly for multi-chromophoric system) is not only originated due to the dielectric properties of the solvent. Rather, the presence of more than one chromophore in close vicinity for highly substituted systems and more flexibility in the side chains in water medium (in comparison with highly viscous DMSO solvent) appear to be the most probable reason for this new absorption, as discussed in the previous section.

The HOMO-LUMO transitions for all the complexes follow the same pattern i.e. $p\pi(Br)\rightarrow\pi^*(L)$ transition except for complex C4, where an ILCT $(\pi\rightarrow\pi^*)$ transition has been observed. Few MLCT transitions at around 288~297 nm have also been observed for C1, C2 and C3 complexes which corresponds to $d(\pi)Re\rightarrow\pi^*(L)$. It should be noted that no such MLCT transitions has been observed for the other two complexes (C4 and C5) containing the tris and tetra (di-2-pyridylaminomethyl)benzene ligands. On the other hand, for C4 and C5, most of the

transitions around 285~293 nm corresponds to ILCT transitions. The absorption behavior of the complexes is almost the same as their respective ligands. All these transitions occurring around 285~297 nm are in well agreement with the experimentally observed results.

Conclusions

The photophysical behavior and excited state relaxation process of strategically substituted flexible di-2-pyridylaminomethyl chromophores on a rigid benzene framework and their corresponding mono-metallic Re(I) complexes were investigated by steady state and time-resolved fluorescence spectroscopy in conjunction with density functional theory calculation. An abrupt break in the transition of fluorescence parameters at low DMSO concentration in DMSO-water binary solvent mixture is apparent in all the systems and explained on the basis of unavailability of water hydrogen bonded network structure at $X_{DMSO} = 0.1 \sim 0.3$. Experimental as well as theoretical calculation results predict spin allowed inter-chromoric interaction and complete reversal in accumulation of electron density on excitation in highly substituted ligand systems, particularly in trimer and tetramer. The results are interesting and can lead towards designing a dendritic architecture similar to artificial photosynthetic antenna system by suitably placing a trapping site along with the di-2-pyridylaminomethyl chromophores as peripheral flexible subunit on the benzene core.

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System	Vol. % water	λ_{Abs} /nm	λ_{Emi} / nm	Δv_{ss} /cm ⁻¹	□ _f /10 ⁻²	$ au_{av}$ /ns	k^{r} /10 ⁶ , s ⁻¹	$\frac{\Sigma k^{nr}}{10^8, s^{-1}}$
L1	0	297	360	5892.3	9.96	1.2	81.5	7.3
	98	308	378	6012.5	0.93	4.4	2.1	2.3
L2	0	300	367	6085.4	3.1	1.3	23.1	7.2
	98	310	410	7867.8	0.4	0.9	4.3	10.7
L3	0	296	356	5693.9	12.61	1.2	103.9	7.2
	98	310	408	7748.3	0.57	2.1	2.7	4.6
L4	0	300	367	6085.4	3.9	1.0	39.9	9.8
	98	310	407	7688	0.02	2.3	8.3	4.3
L5	0	296	355	5614.8	1.72	2.5	6.8	3.9
	98	304	433	9800.0	0.56	2.4	2.3	4.2
C1	0	295	365	6501	0.56	2.2	2.6	4.5
	98	295	355	5729	0.19	5.7	0.3	1.8
C2	0	295	372	7016.6	0.37	3.1	1.2	3.2
	98	295	360	6120.5	0.22	3.0	0.7	3.3
C3	0	295	369	6798.0	2.82	2.0	14.1	4.9
	98	295	366	6575.9	0.73	6.6	1.1	1.5
C4	0	294	364	6541.1	2.25	1.1	20.2	8.7
	98	302	370	6085.6	0.27	4.7	0.6	2.1
C5	0	290	347	5664	0.16	4.2	0.4	2.4
	98	294	350	5442	0.13	4.1	0.3	2.4

Table 1: Spectral properties of the investigated systems in two representative solutions of DMSO-water mixture with varying volume percent of water content.^a

^a The corresponding mole fraction of water for 0 and 98% (ν/ν) water mixtures are 0.00 and 0.99, respectively; λ_{Abs} and λ_{Emi} representing the absorption and emission maximum, respectively; $\Delta \nu_{ss}$ = Stokes shift; \Box_f = fluorescence yield; $\tau_{a\nu}$ = average fluorescence decay time; k^r and Σk^{nr} represent radiative and total non-radiative decay rate constants.

System	Important	Energy Gap	Calculated	Oscillator	Character ^b	Expt.
•	Excitations	$(\Delta E), eV$	λ, (nm)	Strength (f)		λ, (nm)
L1	$H \rightarrow L+2$	4.71	289.12	0.1752		297
	H-1→L	4.94	288.67	0.0237		
C1	H→L	3.78	339.18	0.0003	Br→L1 [LLCT]	
	$H \rightarrow L+2$	4.27	290.28	0.0060	$Br \rightarrow L1 [LLCT]$	295
	H-4→L	4.86	289.57	0.0387	$Re \rightarrow L1[MLCT]$	
	H-1 \rightarrow L+2	4.32	286.64	0.0120	Br→L1 [LLCT]	
L2	$H \rightarrow L+2$	4.73	289.93	0.2607		300
	$H \rightarrow L+4$	5.0	284.78	0.0066		
C2	H→L	3.75	349.35	0.0003	$Br \rightarrow L2[LLCT]$	
	H-3→L+1	4.56	297.08	0.0089	Re→L2[MLCT]	295
	$H \rightarrow L+4$	4.52	289.63	0.1244	Br→L2 [LLCT]	
	H-4→L	4.79	288.41	0.0201	$Re \rightarrow L2[MLCT]$	
L3	$H \rightarrow L+2$	4.78	289.84	0.2626		296
~		0.5		0.0000		
C3	H→L	3.67	338.48	0.0022	$Br \rightarrow L3 [LLCT]$	205
	H-3→L+1	4.50	293.39	0.0271	$Re \rightarrow L3[MLCT]$	295
	H→L+I	3.69	291.02	0.0198	$Br \rightarrow L1 [LLCT]$	
	H→L+6	4.82	289.24	0.2619	Br→L1 [LLCT]	
T A	H→I ⊥3	4 71	289.44	0 19/19		300
LA	H→L+5	4.71	287.44	0.0023		300
	$H_{-1} \rightarrow I_{+4}$	4.90	286.61	0.0025		
		1.27	200.01	0.1075		
C4	H→L	3.53	347.36	0.0013	$L4(A4) \rightarrow L4(A)$ [ILCT]	
	H-1→L+2	4.35	292.67	0.1006	L4(A2)→L4(A4) [ILCT]	294
	H→L+7	4.81	291.37	0.1550	$L4(A4) \rightarrow L4(A4)$ [ILCT]	
	H-3→L+2	4.52	290.46	0.0075	Br→L4 (LLCT)	
	H→L+3	4.36	285.30	0.0078	$L4(A4) \rightarrow L4(A) [ILCT]$	
τ5	H→I ±5	/ 91	290.95	0.0758		296
LJ	$H_1 \rightarrow I \pm 1$	4.51	291.65	0.0736		270
	$H_{-1} \rightarrow I_{+2}$	4.09	291.05	0.0778		
			202.21	0.0270		
C5	H→L	3.85	344.15	0.0001	Br→L5 [LLCT]	
20	H-1→L+8	4.89	290.16	0.1081	$L5(A5) \rightarrow L5(A5)$	290
			= •		[ILCT]	
	H-4→L+2	4.66	288.38	0.0097	$L5(A) \rightarrow L5(A)$ [ILCT]	

Table 2: The energy gap, theoretical and experimental absorption bands, electronic transitions and dominant excitation character for various singlet states of the investigated systems.^a

^aMLCT= Metal to ligand charge transfer, LLCT=Ligand to ligand charge transfer, ILCT= Intra ligand charge transfer; ^bFragment labeling for ILCT is according to Scheme – I.

Figure captions

Chart 1: Structures of the compounds investigated in the present study. Ligands (L) and Re(I) metal coordinated ligands are also shown by line drawing.

Scheme I: Pictorial representations of the ligands (L1-L5). (1) L1: A1=R and A2=A3=A4=A5=H (2) L2: A2=R and A1=A3=A4=A5=H (3) L3: A3=R and A1=A2=A4=A5=H (4) L4: A2=A4=R and A1=A3=H (5) L5, when A2=A3=A5=R and A1=A4=H.

Figure 1: Absorption spectral profile for the substituted (di-2-pyridylaminomethyl)benzene ligands (a) and their Re(I) complexes (b) in pure DMSO and varying proportion of DMSO-water mixtures.

Figure 2: Fluorescence emission spectra of L4 (a) and C4 (b) in DMSO and varying proportion of DMSO-water mixtures. The volume percent of water is 0 (i), 10(ii), 20 (iii), 40 (iv), 50 (v), 60 (vi), 75 (viii) and 98 (viii). Inset: (a) Change in emissive state energy (ΔE , cm⁻¹) of L1 and L3 with varying mole fraction of DMSO; (b) Fluorescence spectra of L5 in 98% water (v/v) with excitation at 300 nm (i) and 375 nm (ii).

Figure 3: Change in fluorescence quantum yield of the ligands (a) and their Re(I) complexes (b) with mole fraction of water (X_{Water}) in DMSO-water mixture.

Figure 4: Time resolved fluorescence decay trace of L5 (a) and C3 (b) in 50% and 98% water (ν/ν) solution, respectively, along with the fitting data (solid line) and instrument response function (IRF). Distribution of weighted residual and autocorrelation function as well as numerical values of reduced chi-square (χ^2) and Durbin-Watson (D.W.) parameters are shown for different fitting models.

Figure 5: Time-resolved fluorescence decay traces of L3 and L4 in some representative solvent systems.

Figure 6: Variation in percentage contribution of the fast and slow decay components in different DMSO-water solvent mixtures for L4 (a) and C1 (b).

Highlights for the paper entitled "Photophysical behavior of systematically substituted (di-2pyridylaminomethyl) benzene ligands and its Re(l) complexes: A combined experimental and theoretical approach" by Mostofa Ataur Rohman, Dipankar Sutradhar, S. Sangilipandi, K. Mohan Rao, Asit K. Chandra, Sivaprasad Mitra.

- > Investigated systems show interesting photophysics in DMSO-water mixture;
- > Inter-chromophoric interaction is present in highly substituted systems;
- > DFT calculation results support the experimental findings;
- Strongly modulated photochemistry at low DMSO content ($X_{DMSO} = 0.1 \sim 0.3$);
- Can lead in designing artificial photosynthetic antenna system by placing suitable trapping site.

Graphical Abstract for the paper entitled "Photophysical behavior of systematically substituted (di-2-pyridylaminomethyl) benzene ligands and its Re(l) complexes: A combined experimental and theoretical approach" by Mostofa Ataur Rohman, Dipankar Sutradhar, S. Sangilipandi, K. Mohan Rao, Asit K. Chandra, Sivaprasad Mitra.



Chart 1



Scheme I



 \mathbf{C}





Figure 2



Figure 3



Figure 4



G



Figure 5



Figure 6

