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## Introduction

Rhenium(1) carbonyl-diamine complexes, reported for the first time by Wrighton and Morse in 1974,<sup>1</sup> have been widely investigated mostly due to their importance for potential applications in catalysis, bioimaging, organic light-emitting diodes, and solar energy conversion.<sup>2–27</sup> These compounds have also been found to be well suited for fundamental studies of photoinduced processes in transition metal complexes. The character of the excited states and thus the photophysical and photochemical properties of these systems can be broadly tuned by structural variations of diamine and ancillary ligands and

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# Carbazole effect on ground- and excited-state properties of rhenium(I) carbonyl complexes with extended *terpy*-like ligands<sup>†</sup>

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The ground- and excited-state properties of three novel complexes [ReCl(CO)<sub>3</sub>(L<sup>*n*</sup>- $\kappa^2$ N)] bearing 2,2':6',2"-terpyridine, 2,6-di(thiazol-2-yl)pyridine and 2,6-di(pyrazin-2-yl)pyridine functionalized with 9-carbazole attached to the central pyridine ring of the triimine core *via* phenylene linkage were investigated by spectroscopic and electrochemical methods and were simulated using density functional theory (DFT) and time-dependent DFT. To get a deeper and broader understanding of structure-property relationships, the designed Re(I) carbonyl complexes were compared with previously reported analogous systems – without any groups attached to the phenyl ring and bearing pyrrolidine instead of 9-carbazole. The results indicated that attachment of the *N*-carbazolyl substituent to the triimine core has less influence on the nature of the triplet excited state of [ReCl(CO)<sub>3</sub>(L<sup>*n*</sup>- $\kappa^2$ N)] than the pyrrolidine group. Additionally, the impact of the ligand structural modifications on the light emission of the Re(I) complexes under external voltage was preliminarily examined with electroluminescence spectra of diodes containing the synthesized new molecules in an active layer.

modulated by the environment. In contrast to polypyridine complexes of other transition ions, the complexes fac-[ReX  $(CO)_3(N^N)$ ] contain a single electron-accepting R-diimine ligand ( $N^{\cap}N$ ), which allows to avoid the problem of excitedelectron localization. The carbonyl ligands of fac-[ReX  $(CO)_3(N^{\cap}N)$ ] act as IR markers of redistribution of electron density upon excitation, while information on the  $N^{n-1}$ ligand is manifested in the UV-Vis spectral region of the transition absorption spectra. Therefore, excited-state dynamics of  $[ReX(CO)_3(N^{\cap}N)]$  can be successfully examined using ultrafast experimental methods such as time-resolved infrared spectroscopy, fluorescence up-conversion methods, time-resolved emission spectroscopy, and transient absorption.<sup>28-34</sup> For [ReX (CO)<sub>3</sub>(bipy)] and [ReX(CO)<sub>3</sub>(phen)], it was found that the optically populated <sup>1</sup>MLCT state undergoes femtosecond intersystem crossing (ISC) forming two triplet states: diimine-localized  $\pi\pi^*$  intraligand (<sup>3</sup>IL) and vibrationally hot {ReCl(CO)<sub>3</sub>}  $\rightarrow$  bpv of <sup>3</sup>MLCT character. The conversion from <sup>3</sup>IL to <sup>3</sup>MLCT occurs on a picosecond time scale, and the formed relaxed <sup>3</sup>MLCT state decays by minor radiative and major nonradiative pathways to the ground state.28,35,36

By introduction of suitable substituents into the diamine core or alteration of the ancillary ligands (X), the nature and energy of the excited states in these systems can be changed. It is possible that LLCT (ligand-to-ligand-charge-transfer), IL (intraligand), and ILCT (intraligand-charge-transfer) excited

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states would be responsible for the photoluminescence of rhenium(1) carbonyl-diamine complexes.<sup>37–45</sup>

In recent years, particular attention has been paid to rhenium(I) carbonyl complexes bearing a diimine ligand of D–A or D– $\pi$ -A type, which gives rise to ILCT transitions originating from the donor orbital localized on the electron-rich group to the diimine-based  $\pi$ \*acceptor orbital and co-occurring with the metal-to-ligand charge transfer (MLCT) excitation in the visible region. Most importantly, these systems were found to exhibit enhanced photo- and electro-luminescence properties relative to unsubstituted (parent) compounds. Generally, it is attributed to a thermal equilibrium between energetically close excited states <sup>3</sup>MLCT and <sup>3</sup>ILCT/<sup>3</sup>IL.<sup>46–62</sup>

Continuing our research on the photophysical properties of rhenium(1) carbonyl complexes with *terpy*-like ligands,<sup>63–69</sup> we present here three novel complexes [ReCl(CO)<sub>3</sub>(L<sup>*n*</sup>- $\kappa^2$ N)] bearing 2,2':6',2''-terpyridine (*terpy*), 2,6-di(thiazol-2-yl)pyridine (*dtpy*) and 2,6-di(pyrazin-2-yl)pyridine (*dtpy*) functionalized with a 9-carbazole unit, attached to the central pyridine ring of the triimine core *via* a phenylene linkage (Scheme 1).

Carbazole, consisting of two benzene rings fused on either side of a pyrrolidine ring, is a molecular block of outstanding importance in organic materials due to strong electron donating properties and excellent hole-transporting abilities.<sup>70-75</sup> The ground- and excited-state properties of 1-3 were investigated by spectroscopic and electrochemical methods, as well as simulated by density functional theory (DFT) and time-dependent DFT. To gain a better understanding of structure-property relationships in these systems, optical and electrochemical properties of 1-3 were analyzed in comparison to previously reported systems - without any groups attached to the phenyl ring (1A-3A) and bearing pyrrolidine instead of carbazole (1B-3B) (Scheme S1<sup>†</sup>).<sup>66</sup> Identification of structure-property correlations is of high importance for the rational design of new light emitting materials with the excited state dynamics for desirable photophysical properties and technological applications.

### **Experimental section**

#### Materials

Pentacarbonyl chlororhenium  $[Re(CO)_5Cl]$  (Sigma Aldrich), poly(9-vinylcarbazole) PVK ( $M_n = 25\,000-50\,000$ ; Sigma



Scheme 1 Re(I) complexes studied in the current work.

Aldrich), poly(3,4-(ethylenedioxy)thiophene):poly-(styrenesulfonate) PEDOT:PSS (0.1–1.0 S cm<sup>-1</sup>) and substrates with pixilated ITO anodes (Ossila), as well as all solvents for synthesis (of reagent grade) and for spectroscopic studies (of HPLC grade) were all commercially available and used without further purification. The films and blends with PVK:PBD (50:50 wt%) on glass substrates as well as all the devices with the following configurations: ITO:PEDOT:PSS/compound/Al and ITO:PEDOT: PSS/PVK:PBD:compound/Al with 15, 2 and 1 wt% complex content in the blend, were prepared according to the method reported in our previous work.  $^{63-66,76,77}$  The ligands  $L^1-L^3$  were prepared according to the modified method reported in our previous studies,  $^{66,77,78-80}$  and detailed synthetic procedures are provided in the ESI.

#### Preparation of $[ReCl(CO)_3(L^n - \kappa^2 N)]$ (1-3)

Re(I) carbonyl complexes were prepared using  $[\text{Re}(\text{CO})_5\text{Cl}]$ (0.10 g, 0.27 mmol) and a suitable  $L^n$  ligand (0.27 mmol) according to the procedure given in our previous work.<sup>68</sup> Argon-saturated acetonitrile solution of a suitable ligand and pentacarbonyl chlororhenium was heated in an autoclave reactor for 20 h at 150 °C and gradually cooled to room temperature for 30 h to induce crystallization. The synthesis resulted in yellow (1) and orange (2, 3) solids (with crystals suitable for X-ray diffraction analysis in the case of 2), washed with chloroform or diethyl ether and air dried.

1. Yield: 70%. IR (KBr, cm<sup>-1</sup>): 2021(vs), 1917(vs) and 1889(vs)  $\nu$ (C=O); 1603(m), 1520(w)  $\nu$ (C=N) and  $\nu$ (C=C). NMR: <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  9.24 (s, 1H, H<sup>B4</sup>), 9.16 (d, J = 8.2 Hz, 1H,  $H^{E4}$ ), 9.09 (d, J = 5.2 Hz, 1H,  $H^{E1}$ ), 8.82 (d, J = 4.3 Hz, 1H,  $H^{A1}$ ), 8.52 (d, J = 8.5 Hz, 2H,  $H^{C2}$ ), 8.42 (t, J = 7.4 Hz, 1H,  $H^{E3}$ ), 8.33 (s, 1H,  $\mathbf{H}^{B2}$ ), 8.28 (d, J = 7.8 Hz, 2H,  $\mathbf{H}^{D5}$ ), 8.08 (t, J = 7.1 Hz, 1H,  $\mathbf{H^{A3}}$ ), 7.96 (d, J = 7.7 Hz, 1H,  $\mathbf{H^{A4}}$ ), 7.91 (d, J = 8.5 Hz, 2H,  $\mathbf{H^{C3}}$ ), 7.80 (t, 1H, H<sup>E2</sup>), 7.65 (t, 1H, H<sup>A2</sup>), 7.53-7.44 (m, 4H, H<sup>D2,D3</sup>), 7.33 (t, J = 7.8 Hz, 2H, H<sup>D4</sup>). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 197.8, 194.5, 191.0 (3CO), 161.5 (C<sup>B1</sup>), 157.8 (C<sup>A5</sup>), 157.2 (C<sup>B5</sup>) 156.3 ( $C^{E5}$ ), 152.7 ( $C^{E1}$ ), 149.7 ( $C^{C4}$ ), 149.2 ( $C^{A1}$ ), 139.9 ( $C^{E3}$ ), 139.8 ( $C^{D1}$ ), 139.2 ( $C^{C1}$ ), 136.9 ( $C^{A3}$ ), 133.6 ( $C^{B3}$ ), 129.8 ( $C^{C2}$ ), 127.5 ( $C^{E2}$ ), 127.1 ( $C^{C3}$ ), 126.4 ( $C^{D3}$ ), 125.5 ( $C^{A2}$ ), 125.2 ( $C^{E4}$ ), 125.0 (C<sup>B2</sup>), 124.4 (C<sup>A4</sup>), 123.0 (C<sup>D6</sup>), 120.7 (C<sup>B4</sup>), 120.6 (C<sup>D4</sup>), 120.4 (C<sup>D5</sup>), 109.7 (C<sup>D2</sup>). Anal. calc. for Re(CO)<sub>3</sub>Cl(N<sub>4</sub>C<sub>33</sub>H<sub>22</sub>) (780.24 g mol<sup>-1</sup>): C 55.42; H 2.84; N 7.18% found: C 55.74; H 2.866; N 7.22%. DSC: I run  $T_{\rm m}$  = 216 °C; II run  $T_{\rm g}$  = 205 °C.

2. Yield: 75%. IR (KBr, cm<sup>-1</sup>): 2021(vs), 1920(vs) and 1895 (vs)  $\nu$ (C=O); 1600(s) and 1522(w)  $\nu$ (C=N) and  $\nu$ (C=C). NMR: <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  9.01 (s, 1H), 8.51 (d, *J* = 8.6 Hz, 2H), 8.44–8.39 (m, 2H), 8.31–8.24 (m, 3H), 8.18 (d, *J* = 3.2 Hz, 1H), 8.11 (d, *J* = 3.1 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H). <sup>13</sup>C NMR not recorded due to insufficient complex solubility. Anal. calc. for [Re(CO)<sub>3</sub>Cl(N<sub>4</sub>S<sub>2</sub>C<sub>29</sub>H<sub>18</sub>)]- $\frac{1}{2}$ (CH<sub>3</sub>CN) (813.05 g mol<sup>-1</sup>): C 48.76; H 2.42; N 7.75; S 7.89% found: C 49.11; H 2.557; N 7.35; S 7.783%. DSC: I run *T*<sub>m</sub> = 210, 233 261 °C; II run *T*<sub>g</sub> = 208 °C.

3. Yield: 65%. IR (KBr, cm<sup>-1</sup>): 2023(vs), 1927(s) and 1907(vs) ν(C=O); 1603(s), 1521(w) ν(C=N) and ν(C=C). NMR: <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.41 (s, 1H), 9.49 (s, 1H), 9.21 (s, 1H), 9.17 (d, J = 2.2 Hz, 1H), 9.01 (d, J = 2.8 Hz, 1H), 8.95 (s, 2H), 8.60–8.54 (m, 3H), 8.29 (d, J = 7.9 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.55–7.46 (m, 4H), 7.35 (t, J = 7.2 Hz, 2H) <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>)  $\delta$  196.60, 194.68, 189.61 (3CO), 158.88, 155.70, 153.52, 151.03, 150.14, 148.02, 147.21, 145.92, 145.41, 144.18, 139.80, 139.60, 133.21, 130.04, 127.28, 126.54, 125.66, 123.13, 121.87, 120.74, 120.58, 109.79, 79.19. Anal. calc. for [Re (CO)<sub>3</sub>Cl(N<sub>6</sub>C<sub>31</sub>H<sub>20</sub>)]- $\frac{1}{2}$ (CHCl<sub>3</sub>) (841.91 g mol<sup>-1</sup>): C 49.22; H 2.45; N 9.98% found: C 49.63; H 2.449; N 10.09%. DSC: I run  $T_m$  = 257, 261 °C with decomposition.

#### Crystal structure determination and refinement

The X-ray diffraction data for 2 were collected using an Oxford Diffraction four-circle diffractometer Gemini A Ultra with an Atlas CCD detector using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. Diffraction data collection, cell refinement and data reduction were performed using CrysAlis<sup>Pro</sup> software.<sup>81</sup> The structure was solved using direct methods in SHELXS and refined by full-matrix least-squares on  $F^2$  using SHELXL-2014.<sup>82</sup> All the non-hydrogen atoms were placed at calculated positions and refined with riding constrains: d(C-H) = 0.93 Å,  $U_{iso}(H) = 1.2U_{eq}(C)$ . Details of the crystallographic data collection, structural determination, and refinement for **2** are given in Table 1 whereas selected bond lengths and angles in comparison with those calculated for **1** and **3** are listed in Table S1, ESI.<sup>†</sup>

Crystallographic data for **2** were deposited with the Cambridge Crystallographic Data Center, CCDC 2044804.†

#### Physical measurements

The IR spectra were measured using a Nicolet iS5 FTIR spectrophotometer ( $4000-400 \text{ cm}^{-1}$ ) in the form of KBr pellets.

The absorption spectra were measured using Thermo Scientific Evolution 220 (solution) and Jasco V570 (solid state as film deposited on a glass substrate and as blends with poly (*N*-vinylcarbazole) (PVK): 2-(4-*tert*-butylphenyl)-5-(4-biphen-ylyl)-1,3,4-oxadiazole (PBD) on a glass substrate).

The NMR spectra were collected (295 K) on a Bruker Avance 400 NMR spectrometer or Bruker Avance 500 NMR spectrometer in dimethyl sulfoxide-d<sup>6</sup> for 1 and 3 and in acetone-d<sup>6</sup> for 2. For  $L^1$  and 1, multidimensional correlation NMR was performed with homonuclear correlation spectroscopy performed using 2D COSY experiments, while heteronuclear correlation spectroscopy was done on the basis of HMQC or HMBC (long-range) experiments.

Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT128n potentiostat. The measurements were investigated in acetonitrile solution (Sigma-Aldrich, HPLC,  $\geq$ 99.8%,  $c = 10^{-3}$  mol L<sup>-1</sup>) using a platinum electrode (diam. 2.0 mm) as the working electrode and 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> (Sigma-Aldrich, 99%) as the electrolyte. Platinum coil and silver wire were used as auxiliary and reference electrode. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were recorded with moderate scan rates equal to

#### Table 1 Crystal data and structure refinement for 2

	2
Empirical formula	C <sub>32</sub> H <sub>18</sub> ClN <sub>4</sub> O <sub>3</sub> ReS <sub>2</sub>
Formula weight	792.27
Т, К	295.0(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions, Å and °	
a	11.5309(5)
b	19.4727(7)
С	14.6172(5
β	106.870(4)
$V, Å^3$	3140.9(2)
Ζ	4
$D_{\rm c}, {\rm g} {\rm cm}^{-3}$	1.675
Absorption coefficient, mm <sup>-1</sup>	4.126
F(000)	1544
Crystal size, mm	0.18 imes 0.14 imes 0.09
$\theta$ range for data collection, °	3.39 to 25.05
Index ranges	$-13 \le h \le 13$
	$-23 \le k \le 18$
	$-17 \le l \le 13$
Reflections collected	13 122
Independent reflections	$5538 \left[ R_{\rm int} = 0.0244 \right]$
Completeness to $2\theta$	99.7
Min. and max. transm.	0.792 and 1.000
Data/restraints/parameters	5538/0/388
Goodness-of-fit on $F^2$	1.058
Final <i>R</i> indices $[I > 2\sigma(I)]$	
$R_1$	0.0255
$wR_2$	0.0554
<i>R</i> indices (all data)	
$R_1$	0.0347
wR <sub>2</sub>	0.0579
Largest diff. peak and hole, e $A^{-3}$	0.753 and -0.460
CCDC number	2044804

 $0.1 \text{ V s}^{-1}$  and  $0.01 \text{ V s}^{-1}$ , respectively. The solution was purged with argon for about 10 min before every measurement. All the results were calibrated on ferrocene (Fc) (internal standard).

Differential scanning calorimetry studies were carried out with the use of TA-DSC 2010 apparatus under a nitrogen atmosphere, with a heating rate of 20 °C min<sup>-1</sup>.

#### Photoluminescence spectra

The emission spectra of samples in the solid state (as powder) and solution were measured on a FLS-980 fluorescence spectrophotometer. The emission spectra at 77 K were measured in an ethanol: methanol (4:1 v/v) matrix frozen with liquid nitrogen. The time-resolved TCSPC measurements were carried out for optically diluted solutions using picosecond pulsed diodes (EPLED 375 nm, EPLED 405 nm) as excitation light sources and PMT (Hamamatsu, R928P, Japan) as a detector, with additional measurement of the IRF for the analysis of a fluorescence decay. The quantum yield of each complex was measured on FLS-980 with the integrating sphere attached. The measurements were taken using direct methods for argon-saturated solutions and powdered samples, with their respective solvents or Spectralon® standard as the reference. The samples were excited at their first excitation maxima and measured with 0.25 nm scan rate, 0.2 dwell time, and 3

scan repetitions. FLS-980 software was used to perform the emission correction and calculation of the quantum yield.

Photoluminescence spectra in the solid state as film and as blends with poly(*N*-vinylcarbazole) (PVK):2-(4-*tert*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) deposited on a glass substrate were collected on a Hitachi F-2500 spectrometer. A precise voltage supply (Gw Instek PSP-405) with the sample fixed to an XYZ stage was applied to collect electroluminescence (EL) spectra, and all the measurements were performed using the procedure reported in our previous work.<sup>76</sup>

#### Singlet oxygen sensitization

The singlet oxygen emission was measured on a FluoTime 300 fluorescence spectrophotometer (PicoQuant, Germany) with a NIR PMT detector (Hamamatsu, H10330-45) equipped with a 1100 nm long-pass filter and additional selected narrow-band filters. The sample absorbance was about 0.1 at the excitation wavelength. The samples were excited at 440 nm with use of a Xe lamp or a 40 MHz picosecond laser diode (LDH-440, PicoQuant). A computer-mounted PCI-board multichannel scaler (NanoHarp 250, PicoQuant) was used for data collection.

#### Nanosecond transient absorption spectra

The nanosecond transient absorption was measured with a system described previously.83 The experiments were carried out in rectangular 1 cm  $\times$  1 cm quartz cells at room temperature. Diluted CH3CL or CH<sub>3</sub>CN solutions of 1 and 1A ( $A_{\lambda}$  = 355 nm: 0.2) were excited at 355 nm and the third harmonic of a Nd:YAG laser pulses (Spectra Physics, Mountain View, CA, USA, model INDI 40-10) was employed as a pump. The 150 W pulsed Xe lamp with a lamp pulser (Applied Photophysics, Surrey, UK), a monochromator (Princeton Instruments, Spectra Pro SP-2357, Acton, MA, USA), and an R955 photomultiplier (Hamamatsu, Japan), powered by a PS-310 power supply (Stanford Research System, Sunnyvale, CA, USA) were used in a monitoring system. The data processing system consisted of real-time acquisition using a digital oscilloscope (WaveRunner 6100A, LeCroy, Chestnut Ridge, NY, USA), which was triggered by a fast photodiode (Thorlabs, DET10 M, ca. 1 ns rise time) and transferred to a computer equipped with software based on LabView 8.0 (National Instruments, Austin, TX, USA) which controlled the timing and acquisition functions of the system.

#### Femtosecond transient absorption

The fs TA spectra were measured using a pump-probe transient absorption spectroscopy system (Ultrafast Systems, Helios) described previously.<sup>84,85</sup> The samples of **1**, **1A**, **1B**, **L**<sup>1</sup>, **L**<sup>1A</sup> and **L**<sup>1B</sup> were prepared in CHCl<sub>3</sub>, with absorbance in the range of 0.2–0.7 in the excitation wavelengths (corresponding to concentrations in the range of  $5 \times 10^{-5}$ –2.5 ×  $10^{-4}$  mol dm<sup>-3</sup> for ligands and  $2.5 \times 10^{-5}$ –2.5 ×  $10^{-4}$  mol dm<sup>-3</sup> for the complexes), and placed in 2 mm path length quartz cells with magnetic stirring. The samples were pumped with 355 nm and 420 nm pulses for **1**, **1A** and **1B**, 355 nm for **L**<sup>1</sup> and **L**<sup>1B</sup> and 320 nm for **L**<sup>1A</sup>. Obtained data were analyzed using the Surface

Xplorer (Ultrafast Systems) software, with corrections for the probe chirp and solvent signal before each analysis. The software allowed to perform Singular Value Deconvolution of the 3D surface into principal components (spectra and kinetics), Global Analysis (lifetimes, with an error of ~10%), and Decay Associated Spectra, DAS, of the detected transients.

#### **Computational details**

The theoretical calculations for geometry optimization, molecular orbital analysis, absorption spectra, ionization potentials, electronic affinities, and reorganization energies were performed using the GAUSSIAN-09 program package<sup>86</sup> at the DFT or TD-DFT level with the PBE1PBE<sup>87,88</sup> hybrid exchangecorrelation functional, and the def2-TZVPD basis set for rhenium and def2-TZVP basis set for other elements<sup>89–91</sup> with a polarizable continuum model (PCM) and acetonitrile as the solvent.<sup>92–94</sup> After optimization of the geometry, vibrational frequencies were calculated to verify the minimum on the potential energy surface.

## **Results and discussion**

#### Synthesis and characterization

Coordination of  $L^1-L^3$  to the {Re(CO)<sub>3</sub>}<sup>+</sup> core was achieved by a well-established procedure, that is refluxing of [Re(CO)<sub>5</sub>Cl] with one equivalent of the corresponding ligand in acetonitrile. The identity and purity of the ligands and Re(I) complexes [ReCl(CO)<sub>3</sub>( $L^{n}$ - $\kappa^{2}N$ )] were confirmed by FT-IR technique (Fig. S1<sup>†</sup>), <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Fig. S2-S7<sup>†</sup>) and elemental analysis. For 1 and L<sup>1</sup>, the full assignment of the signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra was achieved by multidimensional techniques <sup>1</sup>H-<sup>13</sup>C HMBC, <sup>1</sup>H-<sup>13</sup>C HMQC, and <sup>1</sup>H-<sup>1</sup>H COSY (Fig. S2 and S5<sup>†</sup>). Due to the bidentate coordination mode of  $L^1-L^3$ , the protons of the peripheral pyridyl/ thiazolyl/pyrazinyl rings become magnetically inequivalent, and separated signals, each integrated for 1 proton, are observed in the <sup>1</sup>H NMR spectra of 1-3 (Fig. S2-S4<sup>†</sup>). The *facial* arrangement of CO groups in the moiety  $[Re(CO)_3]^+$  is supported by the  $\nu(C \equiv O)$  bands, typical for this geometry set, comprising the sharp intense absorption at higher wavenumbers (2023-2021 cm<sup>-1</sup>) and two overlapping lower-energy ones (1927-1889 cm<sup>-1</sup>) (Fig. S1<sup>†</sup>). The average CO stretching frequencies (1942  $\text{cm}^{-1}$  for 1, 1945  $\text{cm}^{-1}$  for 2 and 1952  $\text{cm}^{-1}$  for 3) indicates a decrease of the overall donor ability (including both  $\sigma$ -donor and  $\pi$ -acceptor contributions) of the chelating ligand in the order  $L^1 > L^2 > L^3$ .<sup>11</sup>

All Re(1) complexes were obtained as crystalline solids with melting temperature ( $T_{\rm m}$ ), identified by DSC measurements, in the range of 210–261 °C (*cf.* Experimental section). Two of them, that is with *terpy* (1) and *dtpy* (2) cores after rapid cooling, can be converted into the amorphous state with the glass transition temperature ( $T_{\rm g}$ ) registered in the second heating scan at 205 and 208 °C, respectively. The Re(1) complex with the *dppy* structure (3) melted with decomposition. The representative DSC thermograms are given in Fig. S8.†



Fig. 1 Molecular structure of 2 with thermal ellipsoids set at 50% probability for non-hydrogen atoms. Selected bond lengths (Å) and angles (°) associated with the Re(I) ion: Re(1)–N(1) 2.153(3), Re(1)–N(2) 2.243(3), Re(1)–C(1) 1.916(4), Re(1)–C(2) 1.906(4), Re(1)–C(3) 1.916(4), Re(1)–C(1) 2.4836(10), N(1)–Re(1)–N(2) 74.37(11), N(1)–Re(1)–C(1) 173.48(13), N(1)–Re(1)–C(2) 96.85(14), N(1)–Re(1)–C(3) 92.26(14), N(2)–Re(1)–C(1) 99.76(13), N(2)–Re(1)–C(2) 169.67(13), C(3)–Re(1)–N(2) 98.38(13), C(1)–Re(1)–C(2) 88.70(16), C(1)–Re(1)–C(3) 91.43(16), C(2)–Re(1)–C(3) 87.24(16), C(3)–Re(1)–C(1) 177.72(12), C(1)–Re(1)–C(1) 90.83(12), C(2)–Re(1)–C(1) 92.47(12), N(1)–Re(1)–C(1) 85.53(8), N(2)–Re(1)–C(1) 81.57(8).

The X-ray crystal structure was obtained for 2, and the perspective view of its molecular structure together with selected bond lengths (Å) and angles (°) associated with the Re(i) ion is shown in Fig. 1.

The rhenium ion of 2 adopts a highly distorted octahedral coordination geometry defined by three facially arranged carbonyl ligands, two nitrogen atoms of the L<sup>2</sup> ligand and chloride ion. A significant distortion from the octahedral geometry, largely reflected in a small bite angle N(2)-Re(1)-N(1) angle of 74.37(11)°, significant enlargement of the C(1)-Re(1)-N(2) angle of 99.76(13)° and elongation of the Re(1)-N(2) bond length to the central pyridine ring [2.243(3) Å] in relation to the Re(1)-N(1) distance to the peripheral thiazole ring [2.153(3) Å], is attributed to the  $\kappa^2$ N-coordination of L<sup>2</sup> and the strong steric interaction of the uncoordinated thiazolyl ring with the carbonyl group C(1)-O(1). The non-coordinated triimine peripheral ring is inclined to the central pyridine at 49.91(14)°, while the dihedral angles between the phenyl ring and central pyridine/carbazole planes are 34.67(19)° and 48.61(14)°, respectively. As can be expected, the carbazole unit is more inclined towards phenyl and central pyridine rings than pyrrolidine in 2B (Table S2†). Additional structural data of 2 are available in the ESI (Tables S1-S3 and Fig. S9-S11<sup>+</sup>).

#### Frontier molecular orbital analysis

To gain better insight into how the *N*-carbazolyl unit introduced into the *terpy*-like ligands influences HOMOs and LUMOs and the HOMO–LUMO gap of  $[\text{ReCl}(\text{CO})_3(\text{L}^n - \kappa^2 \text{N})]$ , the frontier molecular orbitals of **1–3** have been calculated at the DFT/PBE1PBE/def2-TZVPD/def2-TZVP level, and their energies and characters were compared to those of previously reported systems  $[\text{ReCl}(\text{CO})_3(\text{L}^n - \kappa^2 \text{N})]$  without any groups attached to the phenyl ring (1A-3A) and bearing pyrrolidine instead of carbazole (1B-3B).<sup>66</sup>

As a result of introducing the electron-donating 9-carbazole unit, the HOMO energy level rises from -6.44 eV for 1A, -6.46 eV for 2A and -6.57 eV for 3A to -6.08 eV for 1, -6.09 eV for 2 and -6.09 eV for 3, respectively (Fig. 2 and Fig. S12 in ESI<sup>+</sup>). The raised HOMO energy level may indicate better hole-transporting properties of 1-3 compared to the parent complexes 1A-3A.<sup>95-97</sup> In relation to the corresponding 1B-3B, however, the HOMO orbital of the designed complexes (1-3) is more effectively stabilized. The increase of HOMO energy in the following orders 1A < 1 < 1B, 2A < 2 < 2B and 3A < 3 < 3B is accompanied by the increase of the energy difference between the HOMO and HOMO-1. In contrast to 1A-3A, for which the HOMO and HOMO-1 are very close in energy (energy gaps 0.12, 0.13, and 0.12 eV), the HOMO and HOMO-1 orbitals of 1-3 and 1B-3B become more energetically separated, with an energy gap of 0.37, 0.38 and 0.42 eV for 1-3 and 0.70, 0.67 and 0.78 eV for 1B-3B, respectively.

The LUMO level of **1–3** remains almost unchanged relative to that for the corresponding one of **1A–3A**, but it is slightly lowered relative to that of appropriate **1B–3B**. These findings seem to be consistent with better  $\pi$ -delocalization properties of the carbazole relative to pyrrolidine. For all three series, the calculated HOMO–LUMO energy gap decreases in the order **1A** (3.82 eV) > **1** (3.43 eV) > **1B** (3.23 eV), **2A** (3.69 eV) > **2** (3.29 eV) > **2B** (3.12 eV) and **3A** (3.62 eV) > **3** (3.12 eV) > **3B** (2.91 eV).

Upon replacing the pyridyl by thiazolyl or pyrazinyl, the HOMO energy level remains almost unchanged, while the LUMO energy is stabilized in the order  $[{\rm ReCl}({\rm CO})_3({\rm R-}terpy-\kappa^2{\rm N})] < [{\rm ReCl}({\rm CO})_3({\rm R-}dtpy-\kappa^2{\rm N})] < [{\rm ReCl}({\rm CO})_3({\rm R-}dtpy-\kappa^2{\rm N})],$  which leads to the decrease of the HOMO–LUMO energy gap in this sequence (Fig. 3 and Fig. S12, S13†).

For all the Re(I) complexes, the LUMO and LUMO+1 reside on the triimine moiety with partial contribution of  $\pi^*$  orbitals



Fig. 2 Partial molecular orbital energy levels of 1 in comparison with the MO diagrams of the complexes 1A (without any group attached to the phenyl ring) and 1B (bearing pyrrolidine instead of carbazole) (for 2 and 3 see Fig. S12 in the ESI $\dagger$ ).



of the phenyl group (Fig. S14 and S15<sup>†</sup>). A remarkable difference can be noticed in the HOMO character for  $[ReCl(CO)_3(L^n \kappa^2$ N] without any groups attached to the phenyl ring (1A-3A) and HOMO character for  $[ReCl(CO)_3(L^n - \kappa^2 N)]$  bearing carbazole (1-3) or pyrrolidine (1B-3B). For the latter ones (1-3 and 1B-3B), the HOMO is largely defined by the electron-donating substituent (carbazole in 1-3 and pyrrolidine in 1B-3B) and the phenylene linkage, while the HOMO of the parent complexes (1A-3A) is located on the {Re(CO)<sub>3</sub>Cl} unit. Notably, the complexes 1-3 and 1B-3B differ in percentage contribution of the phenylene linkage, which is two times higher for Re(1) complexes with the pyrrolidine group than for those bearing the N-carbazolyl substituent (Fig. S15†). Additional theoretical results, including ionization potentials (IPs), electronic affinities (EAs) and reorganization energies  $(\lambda_{hole} \text{ and } \lambda_{electron})^{95-97}$  for 1-3, 1A-3A and 1B-3B are given in the ESI (Tables S4<sup>†</sup>).

#### Electrochemistry

HOMO and LUMO energy levels and the band gap energy ( $E_g$ ) of 1–3 were also estimated experimentally with cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The studies were performed on a glassy carbon electrode in CH<sub>3</sub>CN with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. The potentials were referenced to the ferrocene/ferrocenium redox couple, and onsets of the first oxidation and reduction waves were used to estimate the values of IP and EA, which can be regarded as closely related to the HOMO and LUMO levels, respectively.<sup>98</sup> The relevant electrochemical data of 1–3 are summarized in Table 2, compared to those for 1A–3A and

**1B-3B** in Table S5,† while Fig. S16† shows the CVs and DPVs for **1–3**.

The first reduction process of 1-3 occurs at similar potentials as for 1A-3A and 1B-3B. Upon replacing pyridyl by thiazolyl or pyrazinyl, the first quasi-reversible wave moves towards more positive values. Additional N- or S-donor atom introduced into the  $\pi$ -deficient trisheterocyclic unit of *dtpy* and *dppy* results in increasing  $\pi$ -acceptor properties of the *dtpy* and dppy ligand and leads to the stabilization of the LUMO level in Re(1) carbonyls bearing 2,6-di(thiazol-2-yl)pyridine and 2,6-di (pyrazin-2-yl)pyridine derivatives relative to those with 2,2':6',2"-terpyridines, which is manifested by the appearance of the first reduction peak at less negative potentials in the order  $[\text{ReCl(CO)}_3(\text{R-terpy-}\kappa^2\text{N})] < [\text{ReCl(CO)}_3(\text{R-dtpy-}\kappa^2\text{N})] <$  $[\text{ReCl}(\text{CO})_3(\text{R-}dppy-\kappa^2\text{N})]$ . Such findings are consistent with the theoretical calculations showing stabilization of the LUMO level in this sequence. It is highly probable that the reduction in 1-3 occurs in the triimine core. Nevertheless, the reduction potentials of 1-3 are slightly affected by the electron-donating substituent attached to the phenyl ring. Introduction of pyrrolidine gives rise to the most negative potential for the first reduction wave in all three series 1A-1-1B, 2A-2-2B, and 3A-3-3B.

The first oxidation peaks of 1–3 occur at potentials comparable to those for the parent complexes (1A–3A), which can imply that they are associated with the oxidation of metal centre  $\text{Re}(I/\Pi)$ .<sup>63,64,66,99</sup> In contrast, the oxidation waves



Fig. 4 UV-Vis spectra of 1–3 in CHCl<sub>3</sub> and CH<sub>3</sub>CN.

Table 2 F	Relevant	electrocl	nemical	data	of	1-	3
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Complex	$E_{\rm red}$ [V]	$E_{\rm red(onset)}$ [V]	$E_{\rm ox}$ [V]	$E_{\rm ox(onset)}$ [V]	EA [eV]	IP [eV]	$E_{\rm g} \left[ {\rm eV}  ight]$
1	$-1.78^{a}$	-1.65	$0.71^{b}$	0.59	-3.45	-5.69	2.24
2	$-1.69^{a}$	-1.59	$0.78^{b}$	0.66	-3.51	-5.76	2.25
3	$-1.46^{a}$	-1.32	$0.69^{b}$	0.55	-3.78	-5.65	1.87

 $IP = -5, 1-E_{ox(onset)}, EA = -5, 1-E_{red(onset)}, E_{g_b} = E_{ox(onset)} - E_{red(onset)}.$  Solution: CH<sub>3</sub>CN, concentration:  $10^{-3}$  mol L<sup>-1</sup>, electrolyte: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>. GC as the working electrode. <sup>*a*</sup> Quasi-reversible.

Table 3 The absorption maxima and molar extinction coefficient values for the complexes  $[ReCl(CO)_3(L^n - \kappa^2 N)]$  (1–3)

Complex	Medium	$\lambda/\mathrm{nm}\left(10^4 \ \varepsilon/\mathrm{dm^3 \ mol^{-1} \ cm^{-1}}\right)$
1	CH <sub>3</sub> CN CHCl	380 (1.52), 338 (1.63), 309 (2.34), 288 (3.63), 237 (6.67) 391 (1.51), 332 (1.67), 310 (2.73), 287 (3.87), 245 (6.46)
2	CH <sub>3</sub> CN CHCl <sub>2</sub>	394 (1.58), 331 (2.44), 287 (3.73), 237 (6.35) 415 (1.47) 337 (2.57) 289 (3.91) 262 (4.03) 246 (5.48)
3	CH <sub>3</sub> CN CHCl <sub>3</sub>	400 (0.47), 336 (0.91), 323 (1.06), 287 (1.43), 237 (2.53) 429 (0.45), 336 (0.99), 324 (1.10), 287 (1.41), 242 (2.93)

observed at much lower potentials of **1B–3B** were assigned to oxidation in the pyrrolidine moiety.<sup>66</sup>

# Absorption spectral behavior and time-dependent DFT calculations

The electronic absorption spectra of **1–3**, registered in two solvents of a different polarity are presented in Fig. 4, and the relevant spectroscopic data for **1–3** and free ligands are summarized in Table 3 (see also ESI, Fig. S17–S19 and Table S6†).

By comparing with the spectra of the free ligands, the high energy absorptions of 1–3 are assigned to the  $\pi \rightarrow \pi^*$  transitions localized on the *terpy*-like ligand coordinated to the metal center in a bidentate mode (Fig. S17†). The longest-wavelength absorptions of 1–3, with maxima in the range 380–429 nm and much lower molar extinction coefficients, possess charge transfer character. With the increase of the solvent polarity from chloroform ( $\varepsilon = 4.8$ ) to acetonitrile ( $\varepsilon =$ 37.5), the band is blue-shifted by 740 cm<sup>-1</sup> for 1, 1284 cm<sup>-1</sup> for 2 and 1690 cm<sup>-1</sup> for 3 (see Table 3). Referring to the previous studies, the negative solvatochromic effect seems to be typical of MLCT excited states in these systems.<sup>3,100,101</sup>

Expectedly, the replacement of the *terpy* core by *dtpy* and *dppy* leads to the shift of the lowest energy band towards the red end of the spectrum. This effect, observed also in the solid (Fig. S19†), is attributed to the increase of ligand  $\pi$ -acceptor properties owing to the introduction of additional donor atoms into peripheral rings (S in *dtpy* and N in *dppy*). On the



Fig. 5 UV-Vis spectroscopy properties of 1 in comparison to the spectral profiles of 1A and 1B in CHCl<sub>3</sub> and CH<sub>3</sub>CN.



Fig. 6 Experimental (red line) absorption spectra of 1-3 in CH<sub>3</sub>CN alongside with transitions (black lines) computed at the TD-DFT/PCM/ PBE1PBE/def2-TZVPD/def2-TZVP level with the use of the PCM model at polarities corresponding to CH<sub>3</sub>CN.

other hand, comparative analysis of absorption spectral profiles of 1–3 with those for 1A–3A and 1B–3B, illustrated in Fig. 5 and Fig. S18,† shows that the appended *N*-carbazolyl unit does not alter the energy of the longest-wavelength absorption relative to the appropriate one of 1A–3A, but results in a significant increase in its molar absorption coefficient. In relation to the Re(1) complexes with ligands bearing pyrrolidine instead of the 9-carbazole group (1B–3B), the long-wave absorption of 1–3 is more symmetrical, less intense, and appears at a higher energy, which may indicate minor contribution of intraligand charge-transfer (ILCT) transitions from the donor orbital localized on the 9-carbazole to the triiminebased  $\pi^*$  acceptor orbital than from pyrrolidine to the triimine acceptor.

To gain insight into the nature of the excited states of 1-3, the computational studies at the TD-DFT/PCM/PBE1PBE/def2-TZVPD/def2-TZVP level were undertaken (Fig. 6). According to the theoretical calculations, the low-energy absorption band of 1-3 is composed of several transitions of different origins (Fig. S20 and Table S7<sup>†</sup>), but predominant contribution can be assigned to the excitations HOMO  $\rightarrow$  LUMO, HOMO  $\rightarrow$ LUMO+1 and HOMO-1  $\rightarrow$  LUMO for complexes 1-2, and HOMO  $\rightarrow$  LUMO, HOMO  $\rightarrow$  LUMO+1 and HOMO-2  $\rightarrow$  LUMO for 3. Based on the MO composition, the transitions HOMO-1  $\rightarrow$  LUMO for 1 and 2 and HOMO-2  $\rightarrow$  LUMO for 3 can be allocated as <sup>1</sup>MLCT [ $d_{\pi}(Re) \rightarrow \pi^{*}(triimine)$ ], while HOMO  $\rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO+1 are best described as charge transfer with electronic density originating from the 9-carbazole donor unit to the  $\pi$ -conjugated triimine acceptor moiety (<sup>1</sup>ILCT). Therefore, the low-energy absorption band of 1-3 can be assigned to a combination of <sup>1</sup>ILCT and <sup>1</sup>MLCT transitions.

In accordance with the experimental data, the calculated low energy excitations for 1–3 fall in the same energy range as for 1A–3A, but they are blue-shifted relative to those for 1B–3B of predominant ILCT character. Higher oscillator strength values for the calculated low energy excitations of 1–3 in relation to those for 1A–3A correlate with a significant increase in molar absorption coefficients of the low-energy absorption bands of 1–3.

#### Luminescence

The photoluminescence (PL) and electroluminescence (EL) capacity of the synthesized molecules was tested. PL properties of designed Re(1) complexes (1-3) were investigated in non-polar and polar solvents (CHCl<sub>3</sub>,  $\varepsilon$  = 4.8 and MeCN,  $\varepsilon$  = 37.5), in low temperature glasses, in the form of a thin film on glass substrates, and as blend with poly(N-vinylcarbazole) (PVK) (50 wt%): 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4oxadiazole (PBD) (50 wt%) with various Re(1) complex content in a matrix (1, 2 and 15 wt%) (Tables 4, S8, S9 and Fig. S21-S23 in the ESI<sup>†</sup>). Following photoexcitation at the energetically lowest absorption band, the solutions of 1-3 exhibited emission with maxima falling in the range of 651-738 nm (Fig. 7a). Typically for a vast majority of rhenium(1) carbonyls with terpy-like ligands, the complexes 1-3 have nanosecond lifetimes and low emission quantum yield in solution at room temperature (from 0.51% to 1.39%).<sup>63-69,102</sup> Due to some overlap of the ligand-localized absorptions with those of the MLCT transitions, excitation of 1 in CHCl<sub>3</sub> does not selectively excite MLCT. The residual ligand fluorescence emission, observed as a shoulder at 506 nm, may indicate incomplete energy transfer occurring from the <sup>1</sup>ILCT/<sup>1</sup>IL to <sup>1</sup>MLCT excited state.<sup>103,104</sup> A similar trend was also reported for 1B.66

The frozen-state (77 K) emission of 1–3 appears in the higher energy region (540–581 nm) due to the rigidochromic effect,  $^{43,105}$  and is characterised by lifetimes in microseconds (Table 4 and Table S8†). Except for 1 at 77 K, the emission of designed complexes is structureless, which may indicate the charge transfer character of the excited state. A weak vibronic structure observed in the emission spectrum of 1 at low temperature may arise due to some degree of mixing between <sup>3</sup>CT and <sup>3</sup>IL/ILCT excited states (Fig. 7b).<sup>3,106</sup>

Taking into consideration the triimine skeleton, it can be noticed that the emission of the Re(1) complex with the 2,2':6',2"-terpyridine-based ligand (1) appears at a significantly higher energy in relation to that for 2 and 3, both in solution and in a matrix at low temperature. The solid state emission of the designed complexes systematically moves towards the red

Fable 4         Summary of photoluminescence properties	of <b>1</b> –	3
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Complex	Medium	Excitation	Emission	Lifetime [ns]	$\chi^2$	φ[%]
1	MeCN	370, 326, 282, 254	651	0.58 (13.33%), 2.60 (86.67%)	0.955	0.58
	CHCl <sub>3</sub>	385, 316, 287, 261	506 657	7.74 (76.77%), 2.90 (23.23%) 3.17 (73.15%), 7.66 (26.85%)	$1.044 \\ 1.052$	1.39
	77 K (EtOH : MeOH 4 : 1 v/v)	400, 322, 289, 278, 240	513, 540	9874 (41.66%), 38 355 (58.34%)	1.080	_
	Solid	486	596	332.71	0.958	15.42
2	MeCN	386, 334, 304, 253	733	3.98	0.961	0.92
	CHCl <sub>3</sub>	410, 334, 265	734	5.78	1.086	0.77
	77 K (EtOH : MeOH 4 : 1 v/v)	402, 327, 287, 239	578	2635 (56.68%), 9826 (43.32%)	1.131	_
	Solid	494	618	46.67 (38.05%); 300.57 (61.95%)	1.076	7.55
3	MeCN	400, 322, 288	734	3.35	0.996	0.51
	CHCl <sub>3</sub>	411, 326, 287, 259	738	3.95 (53.05%), 9.26 (46.95%)	1.016	0.99
	77 K (EtOH : MeOH 4 : 1 v/v)	421, 331, 288	578	29 376 (52.62%), 156 554 (47.38%)	1.126	_
	Solid	512	638	30.44 (21.47%); 114.69 (78.53%)	1.000	8.60



**Fig. 7** Normalized emission spectra of 1-3 in solution at room temperature (a), in a low temperature matrix (77 K in EtOH–MeOH (4:1 v/v)) (b), solid state as powder (c), and in film (d).

end in the order 1 (596 nm) < 2 (618 nm) < 3 (638 nm) (Fig. 7c), except for complex 1 in film (Fig. 7d). The bathochromic shift is accompanied by the shortening of the lifetimes (332.7 ns for 1 > 204.0 ns for 2 > 96.6 ns for 3), in accord with the energy gap law.<sup>3,107</sup>

Compared to the recently reported tricarbonyl rhenium(I) of 2-pyridyl-1,2,*n*-triazole complexes (pyta) bidentate ligands,<sup>108,109</sup> the lifetimes of **1–3** are shorter, but their values, markedly increased in relation to those in solutions, are indicative that the nature of solid-state emission is largely of phosphorescence origin. To examine whether the observed increase of the quantum yields of 1-3 in the solid state relative to those in solutions can be assigned to aggregation induced emission phenomenon, the emission spectra of 1-3 in mixtures of acetonitrile and water were recorded. As shown in Fig. 8, for mixtures with water fraction  $(f_w)$  above 70%, the emission wavelength of 1-3 moves towards higher energy and luminescence intensity significantly increases, which can be assigned to the phosphorescence emission upon aggregation (AIPE) effect.<sup>109</sup> In the case of mixtures with water fraction below 50%, the emission maxima of 1 and 3 show bathochromic shifts accompanied by a noticeable luminescence intensity decrease. These findings can be explained by the fact that water as a polar solvent stabilizes the ILCT excited state and simultaneously decreases the luminescence intensity, which is in agreement with the decrease of quantum yield of 1 and 3 upon going from chloroform to acetonitrile solution (Table 4).

To better understand the impact of the *N*-carbazolyl group on the emission properties of  $[\text{ReCl}(\text{CO})_3(\text{L}^n-\kappa^2\text{N})]$ , the photophysical data of **1–3** were analysed by comparison to those for parent complexes (**1A–3A**) and those bearing pyrrolidine instead of carbazole (**1B–3B**).

Noteworthy, different trends can be noticed for appropriate compounds belonging to the series **1A-3A**, **1–3** and **1B–3B** depending on the environment. For matrices at low temperature, the emission of **1–3** covers the range similar to that of **1A–3A**, while the appropriate complex from the series **1B–3B** emits in a lower-energy region (Fig. S21 and Table S8 in the ESI†). The same relation is seen for **1A–1–1B** and **3A–3–3B** in acetonitrile



Fig. 8 Emission spectra of 1 in the CH<sub>3</sub>CN/water mixture with different water fractions ( $f_w$ ). (for complexes 2 and 3 see Fig. S24 in the ESI†).

solution, contrary to the compounds 2A-2-2B, for which there is no marked difference in emission energy (Fig. S21 in ESI<sup>+</sup>). In chloroform, the complexes 1B-3B show hypsochromically shifted emission maxima in relation to those of appropriate complexes of the series 1A-3A and 1-3, while the emissions of the latter ones cover almost the same range (Fig. S21<sup>†</sup>). Inspecting the photoluminescence lifetimes of 1-3 at 77 K and in the solid state by comparison with 1A-3A and 1B-3B, it can be noticed that the introduction of the pyrrolidine into terpy/dtpy/dppy skeleton leads to a remarkable increase in lifetimes (Table S8<sup>†</sup>). Given all these considerations, it can be assumed that the excited states of 1-3 are very likely of the MLCT character, similar to the parent complexes 1A-3A. For 1B-3B, the deactivation process seems to be also involved by ILCT excited states, and the involvement of ILCT transitions is increasing with the solvent polarity. Very strongly donating groups lead to a significant lifetime extension of  $[\text{ReCl}(\text{CO})_3(L^n - \kappa^2 N)]$ , which strongly justifies exploring substituent-related modifications in these systems.

Considering that the Re(1) complexes exhibited photoluminescence in the solid state with a significantly higher PL quantum yield compared to the solution, the effect of its chemical structure on capacity for light emission under applied voltage was also preliminarily examined and compared with the previously reported systems **1A** and **1B**<sup>66</sup> (Fig. 9 and Table S10†). The advantage impact of the presence of the terpy core and pyrrolidine unit on the emission of light induced by external voltage was observed.

#### Nano- and femtosecond transient absorption

To further investigate the nature of the excited states in the examined compounds, transient absorption studies in nano-(nTA) and femto-second (fsTA) regimes were performed for the series **1A–1–1B** (Fig. 10 and 13 as well as Fig. S25–S28 in the ESI†).

With reference to the parent complex [ReCl(CO)<sub>3</sub>(bipy)],<sup>35,36,104</sup> we can safely assume that the formation of the triplet states of **1A**, **1** and **1B** occurs at the ultrafast time delay. Formation of the triplet excited-states in **1A**, **1** and **1B** was additionally evidenced by singlet oxygen photoluminescence in the near-IR at 1270 nm (Fig. 11).

Noteworthy, the fsTA spectra of **1** and **1A** resemble each other and they display very similar TA features to the complex  $[\text{ReCl}(\text{CO})_3(\text{bipy})]$ .<sup>35,36,104</sup> The ESA band at ~370 nm for **1A** and ~355 nm for **1** is characteristic of transitions localized on the bpy<sup>-</sup> core. In the case of **1**, this band is slightly blue shifted due to the introduction of the electron-donating 9-carbazole. The broad bands in the visible region of TA spectra of **1** and **1A** correspond to  $\text{Cl/L}^{---} \rightarrow \text{Re}$  (Ligand-to-Metal-Charge-Transfer, LMCT) transitions coupled with reorganization of electron density within the {ReCl(CO)<sub>3</sub>} moiety. A slight red-shift of the visible ESA band of **1** relative to **1A** corresponds to increasing structural  $\pi$ -conjugation due to the attachment of the 9- carbazole group. An additional component in the decay associated spectrum of **1** (Fig. 10b, 15.7 ps) relative to **1A** is supportive for the involvement of the <sup>3</sup>ILCT/<sup>3</sup>IL configuration



Fig. 9 EL spectra of the selected diodes containing Re(I) complexes: ITO/PEDOT:PSS/complex/Al and ITO/PEDOT:PSS/PVK:PBD:complex/Al for 1 (a); ITO/PEDOT:PSS/PVK:PBD:complex/Al for 1, 2 and 3 with complex content in blend of 1% (b), 2% (c) and 15% (d). All spectra are scaled to the left Y axis, except for the blue spectrum on graph (a) ITO/PEDOT:PSS/1/Al (15 V), which is referenced on the right Y axis.



Fig. 10 Femtosecond transient absorption spectra at selected delay times (a) together with decay associated spectra (DAS) (b) for 1 and 1A.



Fig. 11 Singlet oxygen generation of complexes 1, 1A and 1B. Data for complex 1B taken from ref. 66.

in the emitting state of 1. The lifetimes deduced from the decay of the TA signals of the both complexes (3.1 ns for 1 and 3.9 ns for 1A) appear to be the same within experimental error, and they are essentially the same as those obtained from the decay of emission (3.2 ns for 1 and 3.3 ns for 1A), indicating that emitting excited states can be observed in the TA states of <sup>3</sup>MLCT character (Tables S11 and S12<sup>†</sup>). Nanosecond transient absorption spectra of 1 are shown in Fig. 12. The line shape of the relaxed excited-states spectral feature in the fsTA regime quantitatively matches the nanosecond TA difference spectra, indicating that there are no additional excited states observed between the femtosecond and nanosecond time domains. Observed nanosecond transient absorptions, due to their short lifetimes (basically comparable to the laser pulse duration of ca. 10 ns) could be attributed to the  $S_1 \rightarrow S_n$  transitions. However, taking into consideration strong resemblance to [ReCl(CO)<sub>3</sub>(bipy)], for which intersystem crossing occurs at the ultrafast time delay,<sup>35,36,104</sup> as well as the fact that short <sup>3</sup>MLCT lifetimes (from 0.58 to 2.3 ns) were recently evidenced



Fig. 12 Nanosecond transient absorption spectra of CH<sub>3</sub>CN and 1 in CH<sub>3</sub>CN and CHCl<sub>3</sub> (a); the nsTA decay kinetics at 400 nm for 1 (b) (for complexes 1A and 1B see Fig. S25 in the ESI<sup>†</sup>).

in related rhenium(1)  $\kappa^2$ N-tricarbonyl complexes with 4'-(4-substituted-phenyl)-terpyridine ligands using transient IR spectroscopy (TRIR),<sup>102</sup> they seem to be rather of <sup>3</sup>MLCT origin. On the other hand, the compounds 1 and 1A were found to generate singlet oxygen with a moderately high yield (Fig. 11), and this generation requires a contribution of longer-lived triplet excited state. As confirmed by kinetic fit (Fig. 12b), the dark triplet T<sub>1</sub>  $\rightarrow$  T<sub>n</sub> absorption of the <sup>3</sup>IL/<sup>3</sup>ILCT character with lifetime ~28 µs is overlapped with the ground state absorption.

The attachment of pyrrolidine resulted in the appearance of the clear bleaching at the wavelength ( $\sim$ 425 nm) that was in

accordance with <sup>1</sup>MLCT/<sup>1</sup>ILCT of **1B**, significant red-shift of the broad bands in the visible region of TA spectra and substantial increase in the TA triplet lifetime relative to **1** and model complex **1A** (Fig. 13). Determined using nTA spectroscopy lifetimes of **1B** in argon-saturated and air-saturated acetonitrile solutions are 774 and 162 ns, respectively.<sup>66</sup> The most reasonable explanation of these observations is significant mixing of <sup>3</sup>MLCT and <sup>3</sup>ILCT/<sup>3</sup>IL excited states, supported also by PL studies.<sup>110–112</sup> The <sup>3</sup>MLCT energy in the complex **1B** was estimated to be 18 421 cm<sup>-1</sup>, while the triplet energy of the free ligand was *ca.* 21 000 cm<sup>-1</sup>. In the case of **1**, the



Fig. 13 Femtosecond transient absorption spectra at select delay times (a) together with decay associated spectra (DAS) (b) for 1B and L<sup>1B</sup>.

 ${}^{3}$ ILCT/ ${}^{3}$ IL state is energetically higher and its population from  ${}^{3}$ MLCT is inefficient. The energies of  ${}^{3}$ MLCT and  ${}^{3}$ ILCT/ ${}^{3}$ IL in 1 were estimated to be 18 611 cm<sup>-1</sup> and 23 732 cm<sup>-1</sup>, respectively (Fig. S29 and S30†).

Additional data concerning transient absorption studies in nano- and femto-second regimes for **1A**, **1** and **1B** are available in the ESI (Fig. S25–S28 and Tables S11–S14†).

## Conclusions

Three novel complexes [ReCl(CO)<sub>3</sub>( $L^n$ - $\kappa^2$ N)] bearing 2,2':6',2''terpyridine, 2,6-di(thiazol-2-yl)pyridine and 2,6-di(pyrazin-2-yl)pyridine functionalized with 9-carbazole attached to the central pyridine ring of the triimine core via phenylene linkage were synthetized. All the complexes were characterized electrochemically and photophysically. Their ground- and excited-state properties were compared with those of previously reported analogous systems - without any group attached to the phenyl ring and bearing pyrrolidine instead of 9-carbazole. It was evidenced that the introduction of the electron-donating 9-carbazole unit did not alter noticeably the energy of the longest-wavelength absorption relative to the corresponding parent complex. Due to the <sup>1</sup>ILCT involvement, only substantial increase of molar absorption coefficients was confirmed. The attachment of 9-carbazole to the triimine ligand did not lead to a switch in the nature of the lowestlying triplet excited state. TA spectra of the [ReCl(CO)<sub>3</sub>( $L^{1}$ - $\kappa^{2}N$ )] showed high similarity to those of the parent complex  $[\text{ReCl}(\text{CO})_3(4'-\text{Ph-terpy-}\kappa^2\text{N})]$  and related  $[\text{ReCl}(\text{CO})_3(\text{bipy})]$ . It was observed that the presence of the *dppy* unit in complex (3) raises the melting temperature to from ca. 210 °C (1 and 2) to 260 °C, but together with melting the thermal decomposition is seen. Additionally, the compounds with terpy (1) and dtpy (2) core can be converted into stable amorphous material with high  $T_{\rm g}$  (ca. 200 °C), which can give opportunity for the preparation of uniform amorphous thin films. It should be noticed that the all investigated complexes exhibited photoluminescence in the solid state. The replacements of dppy (3) and dtpy (2) with terpy (1) resulted in the highest PL quantum yield in the solid state and emission of light under external voltage by a diode with a neat 1 applied as the active layer. Moreover, the guest-host device based on the complex with the terpy (1) unit showed the most intense EL. It was found that substitution of the phenyl ring in the triimine core and the replacement the carbazole substituent with the pyrrolidine structure raises the light emission intensity induced by voltage. To rationally design new functional materials with pre-defined photophysical behaviour, further substituentrelated modifications in these systems deserve more exploration.

## Conflicts of interest

There are no conflicts to declare.

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