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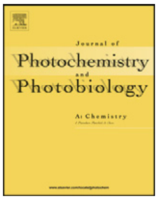

Time-resolved luminescence investigations of the reversible energy transfer from the excited ^{3*}MLCT states to organic acceptors—An alternative method for the determination of triplet state energies and lifetimes

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ABSTRACT

Decays of emission from the excited metal-to-ligand-charge-transfer triplet state (^{3*}MLCT) have been investigated for several luminescent Ir(III) complexes in acetonitrile solutions. Experiments have been performed in the absence as well as in the presence of organic acceptor quenchers (A) having triplet state (^{3*}A) energies close to that characteristic of the ^{3*}MLCT state. This similarity in energies between the ^{3*}MLCT and ^{3*}A states allows observing reversible energy transfer (REN) processes that manifest as changes in the emission decay profiles. In the presence of an organic quencher, the ^{3*}MLCT emission decays change from mono-exponential (characteristic of the excited ^{3*}MLCT state of the investigated complexes) to bi-exponential. The analysis of these observed bi-exponential decays (performed using the Birks' formalism) enables the determination of the kinetic parameters characterizing the investigated forward and backward REN processes. The applied approach is proposed as an alternative method for determining molecular triplet state energies and lifetimes that are sometimes difficult to measure in liquid media.

1. Introduction

Excited state reversible reactions in liquid solution are in some cases difficult to study quantitatively using photophysical methods because of possible small rate constants or short lifetimes of the transient species. Among them, the reversible energy transfer (REN) processes [1–8] have received special attention due to their crucial role in the early stages of photosynthesis and potential technological applications [9]. However, despite their relevance and the extensive experimental and theoretical efforts made so far, there are still remaining fundamental questions regarding the mechanism of the reaction, especially in the case of Dexter type electron exchange [10]. Questions involve the role of the driving force in the REN processes, the role of the solvent viscosity, and the spin states of reactants and products, to name the most important ones. In this respect it was found on several occasions that the dependence on the driving force of the observed quenching rate constant is not trivial, and when irreversible the reaction does not always reach the expected diffusional "plateau" [3,11–13], as was observed in the case of electron transfer processes. [14–16] In order gain greater insight into the observed quenching processes, direct access to the forward and backward rates of the investigated REN is desirable, as has been tempted via transient absorption measurements of the reactants and/or products [17–21].

Unfortunately, often the spectroscopic signals in the former technique are contaminated or the transient spectra are difficult to fully characterize, hindering a quantitative determination of the rate constants [17,20,21]. Time-resolved emission spectroscopy, despite of some limitations, usually offers higher sensitivity and may allow better separation of the signals from different contributions, as in the case of reversible charge transfer [22]. Of course, emission based techniques can be only applied when at least one emitter is involved in the investigated REN process. In order to study a reversible transfer reaction it is also convenient to choose long-lived excited states to ensure sufficient time for equilibration involving *D and *A [23]. Luminescent transition metal complexes exhibiting long-lived (μs) emission from the excited metal-to-ligand-charge-transfer (^{3*}MLCT triplet with emission allowed by spin-orbit coupling) seem to be the obvious choice for such investigations. Not in vain, these species are getting relevant in a huge number of applied areas [24–27].

With a triplet emitter, the spin selection rules impose a triplet state acceptor product. This allows a simple way to determine energies of the excited organic triplets using of triplet transition metal

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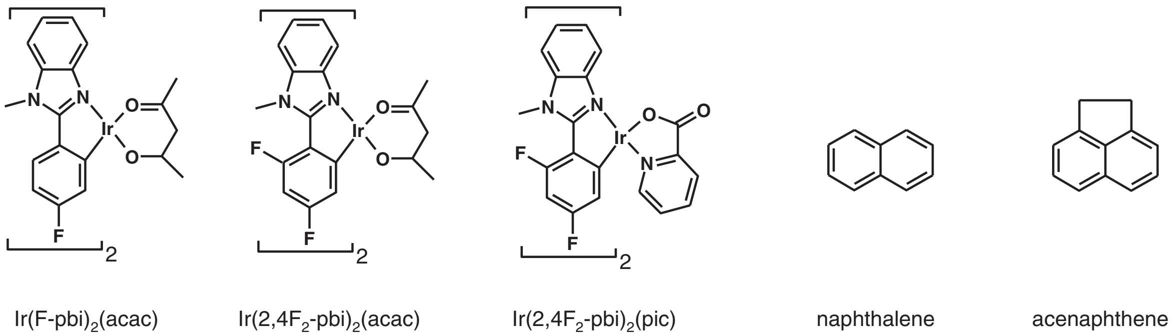

Fig. 1. Structures of the energy donors—cyclometalated Ir(III) complexes and the organic energy acceptors used in this work.

complex donors with well defined triplet energies – i.e., having a structured emission – able to reversibly transfer energy to organic singlet molecules, leading only to their relaxed triplet states. As predicted, and experimentally confirmed, the kinetics of the donor – the triplet transition metal complex – may be bi-exponential in the long time scale [8,17,19–21], and is easily accessible using digital oscilloscopes. Under proper conditions measurements provide both the forward and backward reaction rate constants of the reversible reaction and, by making use of the Gibbs law, the free enthalpy of the REN reaction and finally the energy of ^{3*}A. This approach allows the determination of triplet energies in liquid solution at room temperature of organic compounds that show little or no phosphorescence under such conditions [28]. The relevance of these triplet energies relates to the involvement in important chemical reactions, like the initiation of photo-polymerization [29,30]. Very often they are inferred from low-temperature measurements or can only be obtained by sometimes difficult laser flash photolysis methods [31,32].

Conversely it should be also possible, by employing the same method with an organic acceptor of known triplet energy, to determine the energy of the triplet ^{3*}MLCT state. This may be particularly useful for the transition metal complexes where the classical combination of the steady-state absorption and emission measurements cannot readily be applied because different species (^{1*}MLCT and ^{3*}MLCT, respectively) are involved in the absorption and emission acts. Sometimes it is questionable to extract the energy of the excited ^{3*}MLCT state from room temperature emission spectra because transition metal complexes may exhibit structureless emission spectra.

In this paper we have chosen a group of Ir(III) complexes and organic acceptors of well known characteristics, to test the discussed approach. We have measured the kinetics of the complexes luminescence over different ranges of donor and acceptor concentrations in order to test the accuracy of the proposed method.

2. Experimental

UV–Vis absorption spectra were recorded using a Shimadzu UV2401 spectrophotometer. Luminescence spectra were measured with an Edinburgh Instruments FS900 steady-state fluorometer. Time-resolved measurements were done using a home-built setup with a pulsed PBBO dye laser (emission at 395 nm with energy of 5–6 μJ) pumped by a pulsed nitrogen laser (337 nm, 5 Hz repetition rate, 0.27 mJ) used as excitation source. In a system consisting of any of the iridium complexes here discussed and naphthalene (or acenaphthene), only the iridium complex can be photoexcited by a 395 nm laser (none of the organic acceptors used absorbs at this wavelength). Therefore, it is possible to ascribe unambiguously the role of energy donor to the iridium complex, and of energy acceptor to the naphthalene derivative.

The light emitted by the investigated samples was passed through a monochromator and detected by a Hamamatsu H6780-20 photomultiplier connected to a Tektronix TDS3032 digital oscilloscope. The whole detection system has an instrument response function of ca. 30 ns full width at half-maximum. As usual the measured signal has been regarded as a convolution of the instrument response function and the decay of the excited state of emissive species. The instrument response function of the setup can be reasonably well reproduced by a Gaussian function. The convolution of an exponential decay with a Gaussian function can be performed analytically [33] according to Eq. (1),

$$F(t) = y_0 + \sum_{i=1}^{n} \frac{A_i}{2} \exp\left[\frac{-(t-t_0)}{\tau_i}\right] \times \exp\left[\frac{\Delta^2}{4\tau_i^2}\right] \times \left[1 + erf\left(\frac{(t - t_0 - \Delta^2/2\tau_i)}{\Delta}\right)\right] \quad (1)$$

where the parameters stand for: y_0 the background signal, A_i the normalized amplitudes, t_0 a delay time between the excitation impulse and the recorded decay (due mostly to the color effect [34]), τ_i the lifetimes and Δ is the width of the instrument response function. The difference between the square of this test function with two exponential components to the experimental decay was minimized using a Levenberg–Marquardt Matlab based routine with gaussian weight.

The investigated Ir(III) complexes (Fig. 1), (2,4F$_2$-pbi)$_2$Ir(pic), (2,4F$_2$-pbi)$_2$Ir(acac) and (F-pbi)$_2$Ir(acac), were synthesized and purified as described previously [35,36]. The strongly emissive iridium complexes used as donors, Ir(F-bpi)$_2$(acac), Ir(2,4F$_2$-bpi)$_2$(pic) and Ir(2,4F$_2$-bpi)$_2$(acac), are characterized by emission quantum yields of 0.27, 0.38, and 0.28, respectively and lifetimes of 0.81 μs, 1.87 μs, and 0.88 μs, correspondingly. The excited triplet state energies of the ^{3*}MLCT state of the complexes have been extracted from the maxima of the first emission peak of their structured emission spectra in acetonitrile solutions at room temperature. This may lead to a small underestimation of the ^{3*}MLCT state energies (ca. 0.02–0.03 eV at most).

For the measured systems where naphthalene was the energy acceptor 16 measurements with Ir(2,4F$_2$-bpi)$_2$(pic) complex, 36 measurements with Ir(2,4F$_2$-bpi)$_2$(acac) and 14 measurements with Ir(F-bpi)$_2$(acac) complex have been performed with different combinations of the donor and acceptor. With with acenaphthene as the energy acceptor, 14 measurements for Ir(2,4F$_2$-bpi)$_2$(pic), 14 measurements for Ir(2,4F$_2$-bpi)$_2$(acac), and 8 measurements for Ir(F-bpi)$_2$(acac) complex have been performed. The usual concentration range for donors was 1×10^{-5}–5×10^{-3} M, except for the poorly soluble Ir(2,4F$_2$-bpi)$_2$(pic) complex (about 5×10^{-4} M maximum solubility in acetonitrile solutions). Acceptor concentrations varied typically from 1×10^{-5} to 5×10^{-2} M. All experiments were performed at room temperature (20 °C) in acetonitrile of spectro-

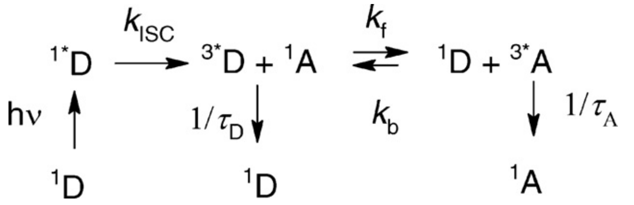

Fig. 2. Kinetic reaction scheme of the reversible energy transfer between a primary excited donor $^{3*}D$ and the excitation energy acceptor A.

scopic purity grade (used as received). The investigated samples were deoxygenated by saturation with purified and dried argon.

3. Results and discussion

In the range of donor and acceptor concentrations used, for a given driving force of the energy transfer reaction around zero, the ^{3*}MLCT emission of the donor should be, and indeed is, clearly bi-exponential. The driving force ΔG_{EN} of the reaction has been calculated (as it was first proposed by Sandros [1]) from the known triplet energy levels of both donor $E_T(D)$ and acceptor $E_T(A)$ for each A and D pair (cf. Table 1) according to:

$$\Delta G_{EN} = E_T(A) - E_T(D) \tag{2}$$

for the reaction scheme in Fig. 2.

In this scheme we have omitted the cage complex formation and dissociation as the reaction in the studied range of energies is kinetically (not diffusionally) controlled. Note that in the case here described, no charged molecules are present nor is charge transferred, hence no work correction (Coulombic attraction or repulsion) terms are needed. The fact that excited state energies can be used for the calculation of a Gibbs free energy has been discussed in the past very clearly [37], and in the present case none of the restrictions to the use of Eq. (2) apply since no large entropic contributions are expected nor are there large molecular deformations respect to the ground state. Note, that there are deviations from Eq. (2) in some cases of ultra-fast energy transfer reactions [38], though it is not the case here. The reaction is spin allowed following the Wigner–Witmer selection rules [39]. It has also to be remarked that in the present case electron transfer reactions are prevented by too large values of ΔG_{ET} (cf. Table 1) as calculated from the redox potentials of the reactants with the Weller equation [40]. It has finally to be borne in mind that the dipole–dipole or Förster [41] energy transfer mechanism is hardly possible because of the very small (if not nil) transition dipole moment for $S_0 \rightarrow T_1$ transitions within the organic acceptors employed.

In absence of energy acceptor, the iridium complexes exhibit mono-exponential decays of phosphorescence independent of their concentration in the range studied and with the laser power employed. In the presence of energy acceptor, however, the systems exhibit bi-exponential decays characterized by two normalized amplitudes (A_1, A_2 with $A_1 + A_2 = 1$) and two decay times (τ_1, τ_2) (cf. Fig. 3).

The kinetic scheme (Fig. 2) can be written in the following system of formal kinetics equations:

$$\frac{d}{dt}[^{3*}D] = -\left(\frac{1}{\tau_D} + k_f[A]\right)[^{3*}D] + k_b[^{3*}A][D] \tag{3a}$$

$$\frac{d}{dt}[^{3*}A] = -\left(\frac{1}{\tau_A} + k_b[D]\right)[^{3*}A] + k_f[^{3*}D][A] \tag{3b}$$

which has been solved by Birks [42] long ago leading to the well known solution for the ^{3*}D decay after pulsed excitation:

$$[^{3*}D] = \frac{[^{3*}D]_0}{\lambda_2 - \lambda_1} \times [(\lambda_2 - k_x)\exp(-\lambda_1 t) + (k_x - \lambda_1)\exp(-\lambda_2 t)] \tag{4}$$

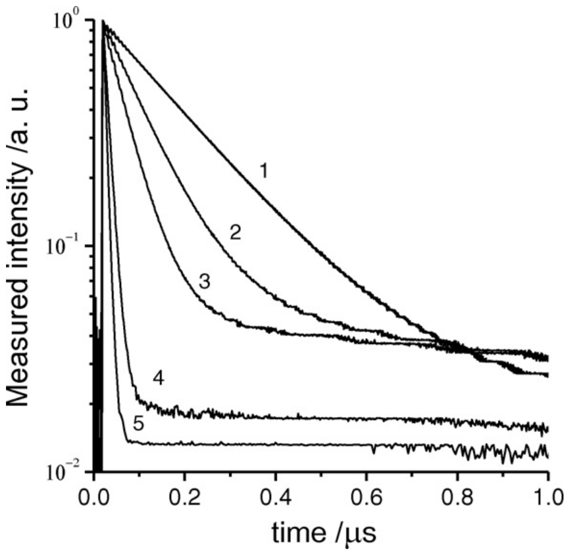

Fig. 3. Time-resolved emission decay of ^{3*}Ir(2,4F$_2$-bpi)$_2$(pic) (1×10^{-4} M) with no added quencher (1) and in the presence of increasing concentrations of naphthalene: 3×10^{-4} M (2), 9×10^{-4} M (3), 5×10^{-3} M (4), and 7×10^{-3} M (5) in deoxygenated acetonitrile. See Experimental section for further details.

where

$$k_y = \frac{1}{\tau_A} + k_b \times [D] \tag{5a}$$

$$k_x = \frac{1}{\tau_D} + k_f \times [A] \tag{5b}$$

and

$$\lambda_{1,2} = \frac{1}{2}\left(k_y + k_x \mp \sqrt{(k_y - k_x)^2 + 4 \times \left(k_y - \frac{1}{\tau_A}\right)\left(k_x - \frac{1}{\tau_D}\right)}\right) \tag{6}$$

Therefore, from a bi-exponential fit to the normalized recorded emission traces, all parameters of interest can be principally determined:

$$\tau_1 = \frac{1}{\lambda_1} \tag{7a}$$

$$\tau_2 = \frac{1}{\lambda_2} \tag{7b}$$

and

$$A_1 = \frac{\lambda_2 - k_x}{\lambda_2 - \lambda_1} \tag{8a}$$

$$A_2 = \frac{k_x - \lambda_1}{\lambda_2 - \lambda_1} \tag{8b}$$

It is convenient to rewrite the equations in the following way to link the Birks' and the extracted amplitudes and decay times from the experiment:

$$k_x = \frac{A_1}{\tau_1} + \frac{A_2}{\tau_2} = \frac{1}{\tau_D} + k_f[A] \tag{9a}$$

and

$$k_y = \frac{A_2}{\tau_1} + \frac{A_1}{\tau_2} = \frac{1}{\tau_A} + k_b[D] \tag{9b}$$

Thus, the plots of the k_x vs. [A] should be linear with origin coordinates $1/\tau_D$ and slope k_f. Correspondingly, the plots of the k_y vs. [D] should be linear as well allowing estimation of $1/\tau_A$ and k_b. Examples fulfilling this expectation are shown for our experiments in Fig. 4 where presentations in doubly logarithmic scale were used for more clarity.

Table 1
Summary of measured reaction rate constants, lifetimes and calculated and measured ΔG_{EN} values for the investigated donor–acceptor systems, as well as the electron transfer energies.

System (donor & acceptor)	$k_f/10^9\ M^{-1}\ s^{-1}$	$k_b/10^9\ M^{-1}\ s^{-1}$	$\tau_D/\mu s$	$\tau_A/\mu s$	ΔG_{EN}/eV (1)	ΔG_{EN}/eV (2)	ΔG_{ET}/eV	
Ir(2,4F$_2$-bpi)$_2$(acac) naphthalene	0.39 ± 0.02	4.89 ± 0.55	0.85 ± 0.04	35.4 ± 53.5	0.105	0.065	1.04	*
Ir(2,4F$_2$-bpi)$_2$(pic) naphthalene	1.26 ± 0.05	2.31 ± 0.11	1.77 ± 0.09	73.9 ± 16.4	0.037	0.015	1.07	0.99
Ir(F-bpi)$_2$(acac) naphthalene	0.36 ± 0.03	4.11 ± 0.23	0.74 ± 0.04	54.6 ± 19.2	0.111	0.062	0.79	*
Ir(2,4F$_2$-bpi)$_2$(acac) acenaphthene	1.35 ± 0.10	2.30 ± 0.20	0.79 ± 0.04	38.9 ± 10.8	0.041	0.014	1.16	*
Ir(2,4F$_2$-bpi)$_2$(pic) acenaphthene	2.20 ± 0.16	0.58 ± 0.05	1.62 ± 0.12	43.6 ± 6.28	−0.027	−0.034	1.25	0.66
Ir(F-bpi)$_2$(acac) acenaphthene	2.01 ± 0.17	2.49 ± 0.01	1.06 ± 0.14	26.6 ± 9.13	0.047	0.006	0.97	*

Lifetimes of the excited ^{3*}MLCT states of iridium complexes (measured directly): Ir(2,4F$_2$-bpi)$_2$(acac) = 0.88 μs, Ir(2,4F$_2$-bpi)$_2$(pic) = 1.87 μs, Ir(F-bpi)$_2$(acac) = 0.81 μs [35,36]. Lifetime of naphthalene excited triplet state = 38 μs from ref. [28]. ΔG_{EN} (1) is the energy of the reaction as calculated from Eq. (2), while ΔG_{EN} (2) is obtained from the rates in the first two columns and Eq. (10). ΔG_{ET} values correspond to both possible ionization processes $^{3*}D + A \leftrightarrows D^+ + A^-$ and $^{3*}D + A \leftrightarrows D^- + A^+$ (left and right columns, respectively) calculated according to the Weller equation using redox potentials values from Refs. [35,36,45].

[*] All complexes containing acac$^-$ anion do not possess a reversible reduction wave, so the second set of ΔG_{ET} values could not be accurately estimated. Because irreversible electrochemical reduction of IrL$_2$(acac) complexes occurs at somewhat more positive potentials than characteristic for their IrL$_2$(pic) counterpart, the appropriate ΔG_{ET} values must be comparable to those calculated for IrL$_2$(pic) – naphthalene or IrL$_2$(pic) – acenaphthene pairs.

In this manner, for the six systems studied we could obtain not only the rate constants for the forward and backward processes but also the lifetimes of the donor and acceptor triplet excited states. All obtained data are compiled in Table 1. In order to check the accuracy of the kinetically obtained ΔG_{EN}, using the Gibbs equation:

$$\Delta G_{EN} = -RT \ln \left[\frac{k_f}{k_b}\right] \tag{10}$$

its value can be compared to the "spectroscopic" value obtained with Eq. (2). As one can see from Table 1, both values do not deviate by more than 0.06 eV (about 500 cm^{-1}) which is indeed a very nice agreement and shows a quite high precision of the measured rate constants. Other check quantities of this methodology are the recovered lifetimes of donor and acceptor excited triplet states. Also from Table 1 it can be read that they are in good correspondence with the independently measured values for the investigated iridium complexes. For the organic acceptors we only consider the naphthalene value, which is neither far from the one recovered by this methodology (55 μs in average as compared to literature value 38 μs [28]). This larger deviation can be understood in view of the limited accessible range of concentrations of donor and acceptor in which well resolved bi-exponential decays with a decent signal to noise ratio and low fitting uncertainty can be obtained. In fact, it is rather difficult to measure such decays at very low reactants concentrations with the small rate constants we are dealing with, concomitant to the small driving force range we are working in. One can expect, however, that application of single photon timing technique may lead to distinct improvement in accuracy of the measurements, especially at extremely low concentration of the investigated donor and acceptor pair. It should be also noted that errors in τ_A estimations only marginally affect the extracted k_f and k_b values. An additional concern is the possible triplet–triplet annihilation either of the donor or the acceptor. We have measured the lifetime of the donor at several concentrations and no deviations from the low concentration lifetime have been observed. The annihilation of the organic acceptor triplet can be ruled out by considering the fact that no systematic deviations of its extracted lifetime or of the rate constants, has been found with the Ir concentration. Neither emission from the acceptor singlet could be observed. All the former is reasonable taking into account the relatively small extinction coefficient of the Ir complexes ($6 \times 10^4\ M^{-1} cm^{-1}$ at most at 395 nm) and the relatively low irradiances used in our experiments.

Finally, it is instructive to represent the rate constants obtained as functions of the ΔG_{EN} of the forward and backward processes. It is shown in Fig. 5 together with data for the energy transfer quenching of the ^{3*}MLCT emission of $^{3*}Ru(bipy)_3{}^{2+}$ complex by several organic acceptors reported by De Carvalho and Gehlen [12], who studied the reaction by means of steady-state quenching experiments. Such comparison becomes possible because at least for $\Delta G_{EN} < -0.2$ eV the measured k_Q values are mostly governed by the forward energy transfer process occurring with a rate constant equal to k_f. This is, however, not the case at $\Delta G_{EN} > -0.2$ eV because the overall quenching rate is affected by the rate constant of the back energy transfer as well as by the lifetime of the acceptor and the donor concentration. Then the approximation $1/\tau_A >> k_D[D]$ [1,3] is in fact very crude and is not applicable for cases in which the donor concentration is large, the lifetime of the acceptor is long and the ΔG_{EN} of the reaction is around zero, as in our study. Instead of the equation used by De Carvalho and Gehlen [12]

$$k_Q = \frac{k_D k_E}{k_{-D} + k_E + k_{-E}} \tag{11}$$

one should use

$$k_Q = \frac{k_D k_E}{k_{-D} + k_E + k_{-E} + k_D k_{-E} \tau_A [D]} \tag{12}$$

which avoids the above mentioned approximation and it is straighforwardly obtained from the same scheme using also the steady-state approximation. In these two equations, k_E and k_{-E} stand for the forward and backward rate constants, respectively and k_D and k_{-D} for the encounter complex(es) formation and dissociation, respectively. This also means that steady-state measurements can be accurate only for systems with fairly negative ΔG_{EN} values. But because in such cases the observed k_Q rates are close to the diffusional limit, it is not very informative to discus k_f vs. ΔG_{EN} relationships. This is an additional reason why the time resolved study of the ^{3*}D decay is superior to the steady-state quenching studies. One can also conclude that time resolved measurements (applicable also for systems with negative values of ΔG_{EN}) are better suited for the full characterization of the investigated class of energy transfer processes. As was recently shown for oxidation potential differences determined via laser photolysis [46], kinetic evaluations similar to those used here may provide greater accuracy than analogous equilibrium (steady-state) measurements for processes with $\Delta G > \pm 0.1$ eV.

On the other hand, from the data presented in Fig. 5 it is seen that the ΔG_{EN} dependence of these reactions do not reach a maximum value identical to the estimated diffusion limited rate constant k_D ($2 \times 10^{10}\ M^{-1}\ s^{-1}$ as calculated for acetonitrile using the Smoluchowski equation under stick boundary conditions for the mutual diffusion coefficient for particles of similar size [43]). As our results roughly (not exactly in the endergonic region since the k_Q values are smaller than the single processes rates as can be expected from Eq. (11)) follow those of De Carvalho and Gehlen and others [11,12] in the common ΔG_{EN} range, it is quite likely that the plateau would

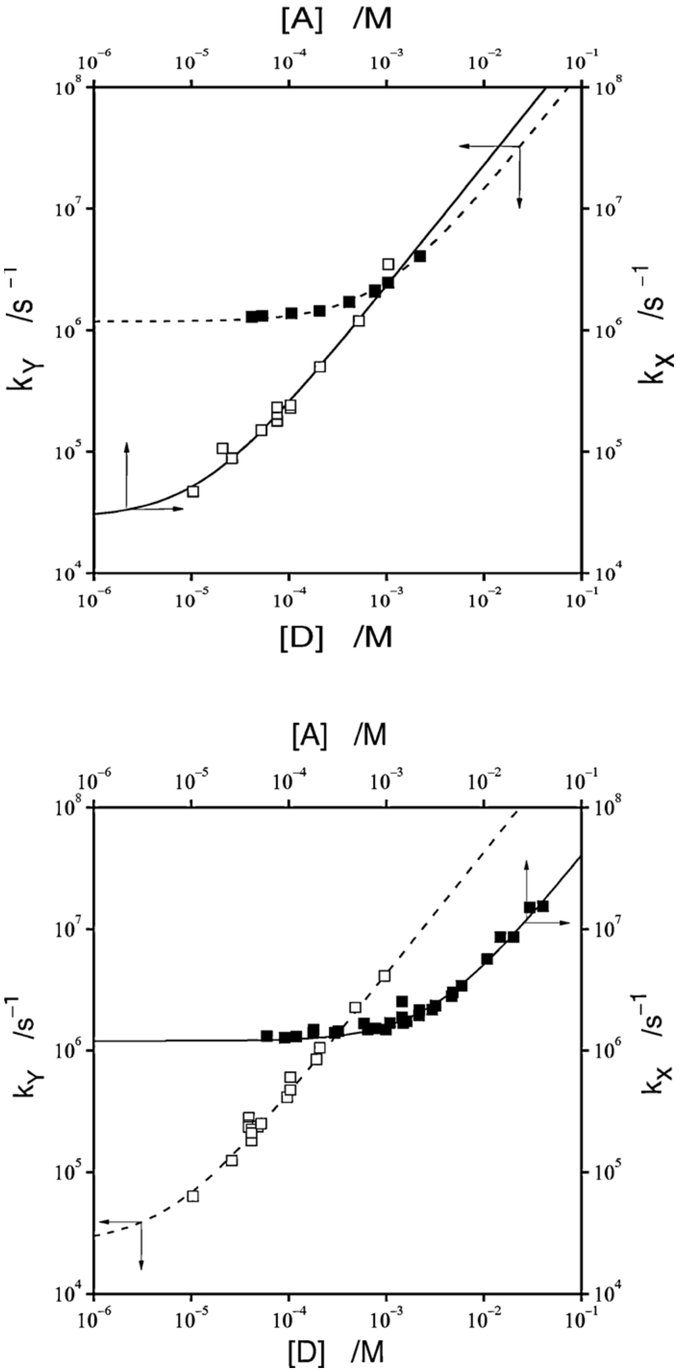

Fig. 4. Birks' model rates (Eqs. (5a) and (5b)) as a function of donor and acceptor concentrations. k_x vs. [A] (open squares) and k_y vs. [D] (filled squares) for two system investigated. The dashed line is the best fit to k_y and the solid line to k_x, respectively. In both cases the slopes are k_f and k_b, respectively and ordinates at the origin of abscissa $1/\tau_a$ and $1/\tau_d$, respectively. Data for Upper panel: Ir(2,4F$_2$-bpi)$_2$(acac) – acenaphthene system. Lower panel: Ir(2,4F$_2$-bpi)$_2$(acac) – naphthalene system.

be also sub-diffusional, suggesting that a kinetic control prevails over the whole free energy range [3]. It is noteworthy that the same trend is observed for the case of 2-nitrothiophene triplet quenching though the data in the latter case are too scattered for a good quantitative comparison [11]. This may indicate that additional factors, like the spin moment in the triplet manifold, may play an important role and keep the reaction kinetically controlled over the whole ΔG_{EN} range. Further studies in our laboratory are in progress to clarify these questions.

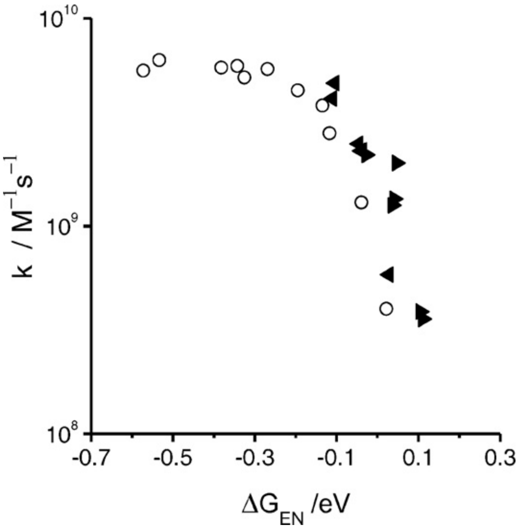

Fig. 5. Dependency of reaction rate constants on ΔG_{EN}. Total quenching rates obtained by steady-state luminescence quenching measurements (○) in reference [12] and time-resolved measurements results of the present work (► for forward rate constant k_f and ◄ for backward rate constant k_b). See Table 1 for the numerical values.

4. Conclusions

The proposed method makes use of time-resolved emission spectroscopy quenching by organic acceptors of triplet phosphorescence from cyclometalated Ir(III) complexes with structured emission. It has been demonstrated that the method can be used accurately to determine the triplet energies of the acceptors as well as their lifetimes. As well, it could be useful for the triplet energy determination of transition metal complexes with non-structured emission. It represents an advantage over more sophisticated methods of transient absorption and in the case of organic triplets that cannot be populated by photo-excitation or do not fully relax in low temperature matrices. This is especially relevant when the organic triplets are involved in chemical reactions used in applied fields as photoinitiators [29,30]. The accuracy of the E_T determination is in the range of 500 cm^{-1} and the lifetimes in the range of tens of μs. Cyclometalated Ir(III) complexes have the additional advantage of showing a large spectral variety covering almost the whole visible spectrum, making it possible to find one for each organic triplet state that would need to be determined. In fact, there are at least a 20 different complexes with structured emission spectra based on Ir(III) that could be used for this purpose expanding over the whole visible spectrum with ^{3*}MLCT energies almost every 0.05 eV [35,36,44].

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