Optically and Electrically Detected Magnetic Resonance Studies of OLEDs and their Implications for Organic Photovoltaics

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Optically and electrically detected magnetic resonance (ODMR and EDMR, respectively) studies of luminescent π-conjugated thin films and OLEDs have provided striking insight into the nature and importance of the various excitations and photophysical processes.[1] The salient feature in the photoluminescence (PL)-detected magnetic resonance (PLDMR) of luminescent π-conjugated polymers (e.g., polythiophenes, poly(*p*-phenylenevinylenes), ladder-type poly(*p*-phenylenes, etc.), and small molecules (e.g., tris(8-hydroxyquinoline) Al) is the *positive* (PL-enhancing) spin 1/2 polaron resonance (Fig. 1).[2,3] Although its nature is still debated, there is very strong evidence that it results from reduced quenching of the luminescent singlet excitons (SEs) by reduced populations of polarons and triplet excitons (TEs). The reduction in the populations of these species is due, in turn, to the well-known strongly spin-dependent quenching of TEs by polarons.[4] This is also plausible due to the simple observation that, under typical steady-state conditions, the populations of these species overwhelms the SE population (by > 100 fold under photoexcitation, by > 10^4 fold under carrier injection).

Although the salient PLDMR in the films is the positive spin 1/2 resonance mentioned above, under sufficiently short wavelength excitation, or under carrier injection in OLEDs, the salient PLDMR and electroluminescence (EL)-detected magnetic resonance (ELDMR) are a *negative* spin 1/2 resonance, respectively (Fig. 2).[3,5,6] In the latter case of OLEDs, a negative electrical current-detected magnetic resonance (EDMR) and photocurrent-detected magnetic resonance (PCDMR) is also observed (Fig. 2).[3,5] Since these negative spin 1/2 resonances were first reported in 1992,[5] they have been assigned to enhanced formation of bipolarons (or trions[7]). Yet their relative effect invariably decreases with increasing current,[3,5] apparently due to saturation of the sites that induce their formation. Hence while these bipolarons and trions are clearly deleterious to the EL, current, and photocurrent in OLEDs, their effect decreases with increasing current.

The negative spin 1/2 EDMR was also observed in ITO/poly(phenyl-phenylene-vinylene) (PPPV)/Al photodiodes,[8] yet it has not been adopted as a major tool in investigating OPVs. In light of recent results by Street, Heeger, and coworkers, which suggest an intrinsic "midgap" state between the highest occupied molecular orbital (HOMO) of poly(3-hexylthiophene) and the lowest unoccupied molecular orbital (LUMO) of [6,6]-phenyl-C_{60}-butyric acid methyl ester (PCBM), the adoption of EDMR and PCDMR to study OPVs appears to be highly desirable.

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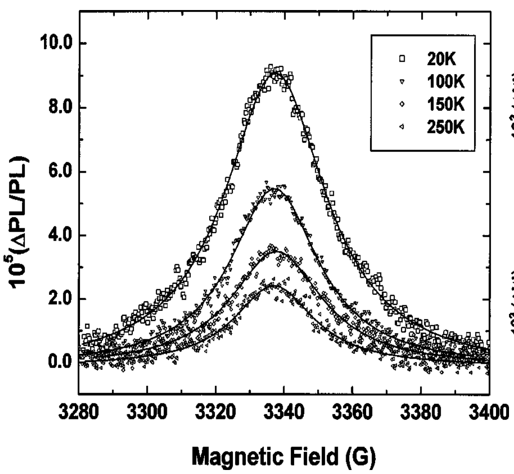

Fig. 1. *The positive spin 1/2 PLDMR in Alq_3 thin films.*[3]

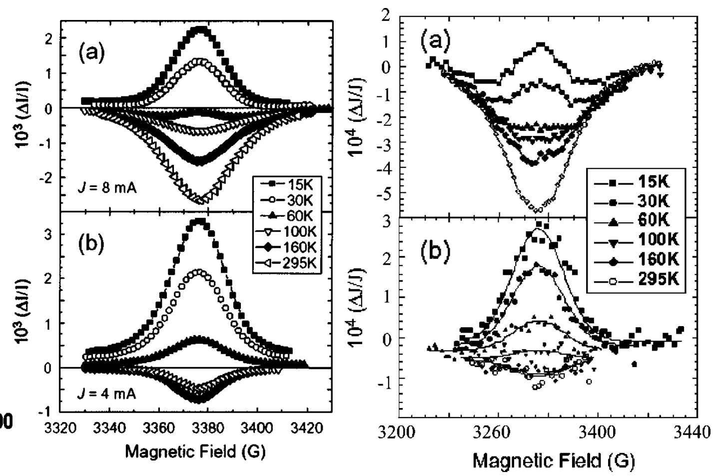

Fig. 2. *The ELDMR (left panels) and EDMR (right panels) in Alq_3 OLEDs with an AlO_x (top panels) and a CsF (bottom panels) buffer layer.*[3]

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