PHYSICAL REVIEW B **76**, 245201 (2007)

Determination of the triplet excited-state absorption cross section in a polyfluorene by energy transfer from a phosphorescent metal complex

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(Received 22 May 2007; published 12 December 2007)

The triplet excited-state ($T_1 \rightarrow T_n$) absorption cross section of poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT) was calculated from quasi-steady-state photoinduced absorption measurements of films of the polymer blended with iridium (III) [(bis 4,6-difluorophenyl)-pyridinato-*N*, C2′] picolinate (FIrpic). Steady-state photoluminescence spectra and photoinduced absorption results showed that quenching of the FIrpic phosphorescence originated from triplet energy transfer from FIrpic to F8BT. By comparing the strength of the photoinduced absorption with the known rate of triplet generation in the F8BT, the triplet excited-state absorption cross section of F8BT was found to be 3.1×10^{-16} cm$^2 \pm 20\%$. This value is relatively small compared with that for poly(*p*-phenylenevinylene)s, but is consistent with previous quantum-chemical calculations. Accurate knowledge of the triplet excited-state absorption cross section is valuable for quantifying the populations of nonemissive triplet excitons in polymer-based devices.

DOI: 10.1103/PhysRevB.76.245201 PACS number(s): 71.20.Rv

I. INTRODUCTION

The formation of triplet excitons can be an important loss mechanism in polymer electronic devices. In polymer light-emitting diodes (LEDs), recombination of injected charge leads to the formation of both singlet and triplet excitons, of which normally only the singlets can decay radiatively. If the recombination process is statistical, only 25% of excitons will be formed as singlets; however, several reports have suggested that this limit may be broken in polymer LEDs.[1–3] The issue remains controversial, largely because it is difficult to quantify the population of nonemissive triplet states in a device.

Although triplet excitons are not radiatively coupled to the ground state, they do have a dipole-allowed transition to a higher-lying triplet state (the $T_1 - T_n$ transition), lying in the near infrared. If the absorption cross section σ_T of this transition is known, the population of triplet states can be calculated from the strength of this absorption. Values of σ_T in the range from 10^{-16} to 2×10^{-15} cm^2 have been estimated in various conjugated polymers,[4–8] but there are few polymers where σ_T is accurately known. Candeias *et al.* have used a pulse radiolysis technique to determine a value of $\sigma_T = 1.6 \times 10^{-15}$ cm$^2 \pm 20\%$ in the poly(*p*-phenylenevinylene) derivative MEH-PPV.[7] Less information is available about values of σ_T in polyfluorenes. Cadby *et al.* have reported a lower limit of $\sigma_T > 2 \times 10^{-16}$ cm^2 in poly(9,9-dioctylfluorene),[6] and ground-state recovery measurements can be used to obtain σ_T when the intersystem crossing efficiency is high.[9]

In an excited-state absorption experiment (photoinduced absorption), the fractional change in transmission $\Delta T/T$ of a probe beam of intensity T at normal incidence is determined by the average density of triplets per unit area, n_A, in the region of the sample probed,

$$\frac{\Delta T}{T} = - n_A \sigma.$$

In the steady state, if the generation rate per unit area is G and the triplets decay monomolecularly with a lifetime τ, then the population is given by $n_A = G\tau$. Thus, if the lifetime and the generation rate are known, it is possible to extract σ_T from the measured photoinduced absorption. Triplet energy transfer from dopant molecules provides a convenient way to determine triplet absorption cross sections.[10] One way to generate triplet excitons in the polymer at a known rate is to add a known amount of a dopant molecule containing heavy metal atoms, where rapid intersystem crossing takes place from singlet to triplet excitons. Photons absorbed in the dopant will thus produce triplet excitons in the system. If the triplet energy of the dopant is higher than the host, then triplet excitons generated on the dopant will transfer onto the polymer, producing a known generation rate of triplet excitons in the polymer. This method has been applied by Cleave *et al.* to find σ_T in OC$_1$C$_{10}$-PPV, using platinum octaethyl porphyrin as the dopant.[8] Here, we use a similar method to find σ_T in the poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT). This green-light-emitting polyfluorene is of particular interest since it gives particularly efficient emission when blended with a hole transporter in light-emitting diodes.[11] Absorptions due to triplet excitons in devices based on F8BT have proven difficult to detect, suggesting that their formation may be suppressed.[12] F8BT has also been used in photovoltaic devices,[13] where triplet exciton formation is also a possible loss mechanism.[14] A value of $\sigma_T \sim 2 \times 10^{-16}$ cm^2 has been calculated for F8BT using time-dependent density functional theory.[14] This value is approximately an order of magnitude lower than the absorption in poly(*p*-phenylenevinylene), a fact that is attributed to the weaker interunit coupling in F8BT. Although these calculations are valuable, the reliability of triplet absorption cross sections predicted using these methods has not yet been tested against experiment. It, therefore, is important to determine σ_T in F8BT experimentally in order to understand fully the working of devices based on this polymer.

The dopant we use here is the phosphorescent material iridium (III) [(bis 4,6-difluorophenyl)-pyridinato-*N*, C2′] picolinate (FIrpic).[15–17] This gives efficient transfer of triplet excitons onto the F8BT, allowing σ_T in F8BT to be measured reliably in a photoinduced absorption measurement.

II. EXPERIMENTAL METHODS

FIrpic was synthesized using literature methods[18] at the Department of Chemistry, Seoul National University, Korea. F8BT was supplied by Cambridge Display Technology Ltd. Films of pure F8BT and its blends with FIrpic were formed by spin coating from chlorobenzene solutions (30 mg/ml) onto Spectrosil-B substrates.

Absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrometer. Room temperature steady-state photoluminescence spectra were detected with a VARIAN Cary Ellipse fluorescence spectrophotometer. Surface topographies of blend films were investigated using an atomic force microscope (AFM) in tapping mode (NanoScope III, Digital Instruments, Inc.).

Photoinduced absorption (PIA) spectroscopy was used to detect the presence of a quasi-steady-state population of triplet excitons in F8BT, due to their absorption at around 1.5 eV. The assignment of this absorption to triplet excitons is well established from previous work,[12,14] which found that triplet lifetime is in the millisecond regime at low temperatures.

The PIA experimental setup has been described in detail elsewhere.[19] For the present work, an argon-ion laser operating in multiline UV mode (351 and 364 nm) was used as the pump source, modulated by a mechanical chopper wheel at 224 Hz. A plano-concave lens was used to diverge the pump beam to an area on the sample that was larger than the probe beam. The beam was measured to have a Gaussian profile with a radius to $1/e^2$ intensity of 4.3 mm. The probe beam was produced by monochromating a 150 W halogen lamp. The size of the probe beam at the sample was approximately $9.8 \times 3.0\ \text{mm}^2$. A second monochromator was used to minimize any luminescence collected, and any remaining luminescence was measured at each wavelength with the probe beam blocked, and subtracted from the signal. A silicon photodiode was used as the detector, and a Stanford SR 830 digital lock-in amplifier was used to measure ΔT in response to the modulated pump beam. All samples were measured in a continuous flow helium cryostat under a low-pressure helium atmosphere.

III. RESULTS AND DISCUSSION

Figure 1 shows the chemical structure, absorption, and photoluminescence (PL) spectra of F8BT and FIrpic at room temperature. The absorption spectrum of FIrpic demonstrates the typical features for a transition metal complex with significant spin-orbit coupling. The absorption bands below 330 nm are attributed to the ligand-centered metal-perturbed bands on the basis of the high extinction coefficients, and bands higher than 330 nm are metal-to-ligand charge-transfer (^{1}MLCT) bands. The PL emission of the FIrpic centered at 475 nm is due to radiative decay from the ^{3}MLCT state to the ground state, whereas the PL emission from F8BT is from singlet excitons.

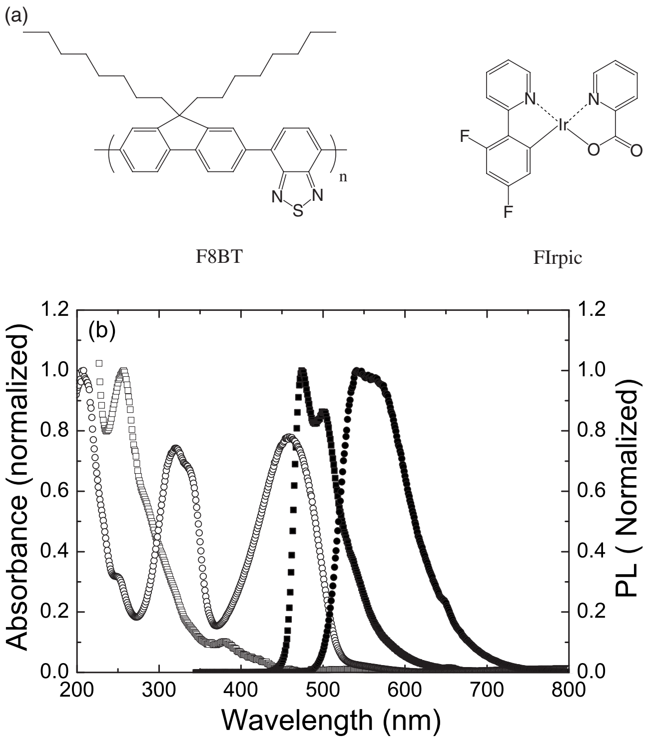

FIG. 1. (a) Chemical structure, (b) absorption and PL spectra of F8BT and FIrpic at room temperature. PL was excited at 325 nm. Absorbance of FIrpic (open squares), absorbance of F8BT (open circles), PL of FIrpic (filled squares), and PL of F8BT (filled circles).

Figure 2 shows the effect on the absorption and PL spectra of blending 5% FIrpic into F8BT. In the blend film, the larger weight in the absorption spectrum at short wavelengths is due to the contribution from the FIrpic. The PL spectra show emission only from the F8BT, with no evidence of any emission from FIrpic. This suggests efficient energy transfer from FIrpic to the polymer.

Figure 3 shows approximate energy levels and possible energy transfer pathways in this system. It is clear that energy transfer from triplet states on FIrpic to triplet states on F8BT (process 3) is energetically possible. Intersystem crossing in FIrpic is very rapid and efficient,[20] as seen by the absence of any singlet emission from pure FIrpic. Singlet energy transfer from FIrpic to the F8BT (process 1) is therefore unlikely. In principle, energy might also transfer from the triplet state of FIrpic to the singlet state of F8BT (process 2). This process can be ruled out by comparing the photoluminescence excitation (PLE) spectrum of the blend with that of the pure F8BT [Fig. 4(a)]. Despite significant contribution to the absorption from the FIrpic at short wavelengths [Fig. 4(b)], the PLE spectra are identical, which indicates that excitation of the FIrpic does not lead to additional singlet states on the F8BT.

To confirm that the lack of FIrpic emission is due to energy transfer to the polymer, we must rule out other possible

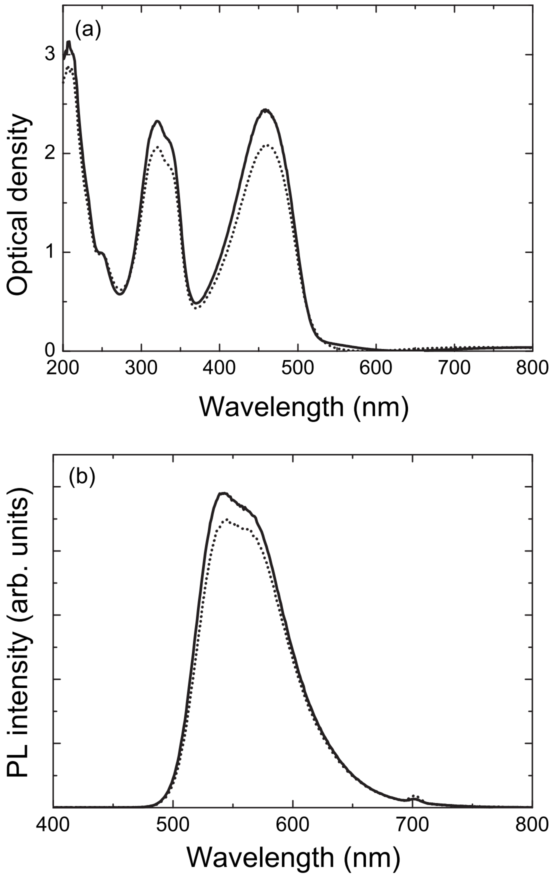

FIG. 2. (a) Absorbance and (b) photoluminescence spectra of pristine F8BT (solid line) and FIrpic(5%)/F8BT blend (dashed line) films. PL was excited at 351 nm.

quenching mechanisms for triplet states. Quenching due to aggregation of the FIrpic can be a problem at high concentrations if chemical incompatibility with the polymer causes phase separation.[21] However, AFM measurements of our blend films (Fig. 5) show that their surfaces are extremely smooth (root mean square surface roughness ~8 Å), which suggests that phase separation is not a problem in our films. Charge transfer at the FIrpic/F8BT interface is another possible quenching mechanism. The ionization potentials of F8BT and FIrpic are 5.9 and 6.0 eV, respectively, and their electron affinities are 3.5 and 3.4 eV, respectively.[22–24] The differences in ionization potentials and electron affinities are small compared with the exciton binding energy, so charge transfer is not likely to occur, either from the singlet or the triplet state. This will be confirmed later by the absence of absorption due to charged species in the PIA experiment.

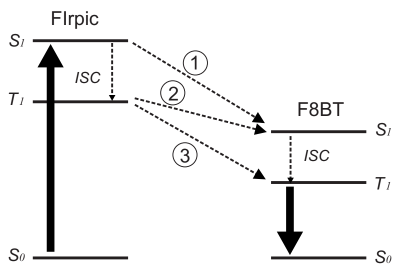

FIG. 3. Approximate energy levels and possible energy transfer paths between F8BT and FIrpic.

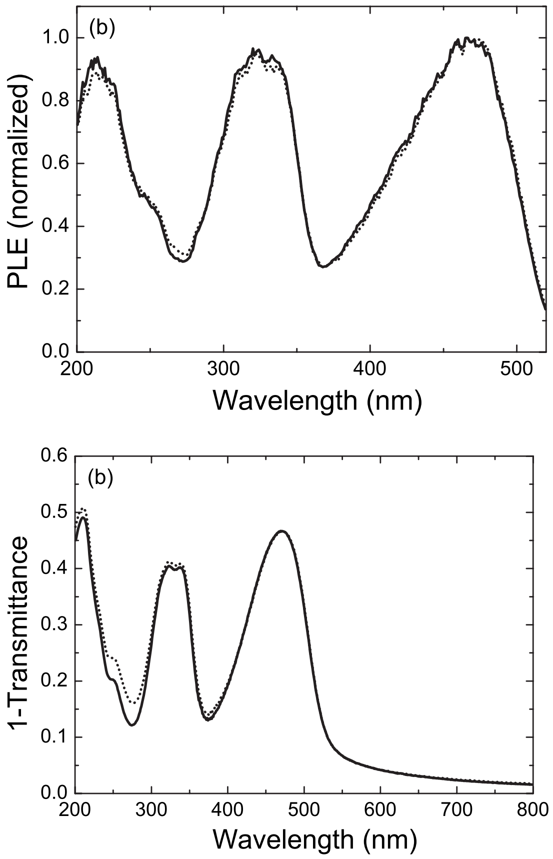

FIG. 4. (a) PLE spectra of thin pristine F8BT (solid line) and FIrpic(5%)/F8BT blend (dashed line) films, with detection at 540 nm. (b) Fractional absorbance of the same films.

Figure 6(a) shows PIA spectra of pristine F8BT and a blend film containing 5% by weight FIrpic in F8BT at 40 K, excited in the UV where both F8BT and FIrpic absorb. The PIA of pristine F8BT shows a broad absorption peak at 845 nm (1.47 eV). No PIA was observed at room temperature. These results are consistent with a T_1-T_n absorption in F8BT, as previously reported.[12,14] These triplet excitons result from intersystem crossing within the F8BT, whereby a small proportion of the photogenerated singlet states is con-

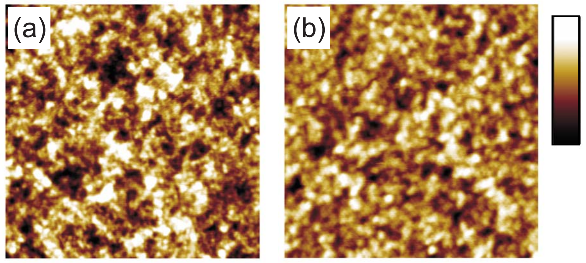

FIG. 5. (Color online) AFM images of the surfaces of (a) pristine F8BT and (b) FIrpic(5%)/F8BT blend films. Image size is 1 $\times 1$ μm^2. Vertical height scale is 5 nm.

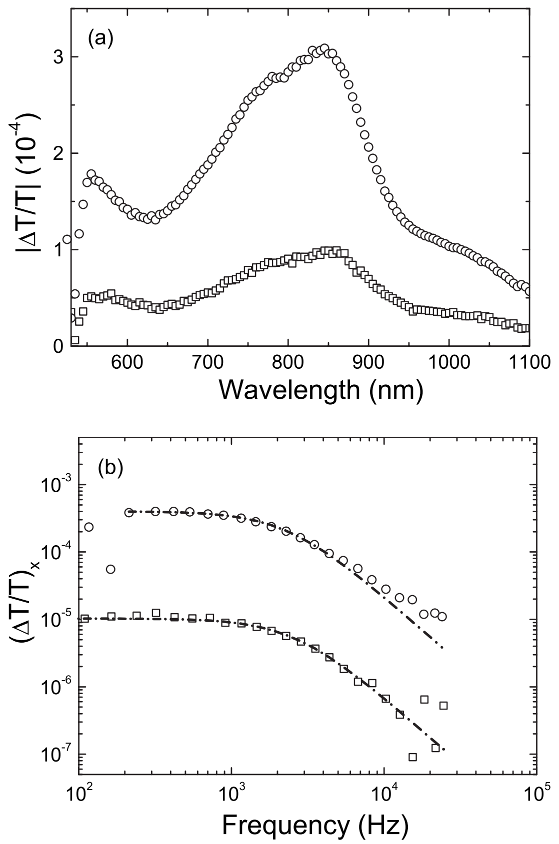

FIG. 6. (a) PIA spectra and (b) chop frequency dependence of the PIA for pristine F8BT (squares) and FIrpic(5%)/F8BT blend (circles) films at 40 K, excited by MLUV.

verted to triplets.[14] The blend films showed a similar shape of PIA spectrum, with no additional features due to charged states. It can be seen that the strength of the $T_1 - T_n$ absorption is increased in the blend film, providing qualitative evidence for the presence of an additional population of triplet excitons in the polymer formed by energy transfer from FIrpic. We note that no additional features due to triplets on FIrpic are observed. The triplet lifetime of FIrpic is short (~1 and ~50 μs at room and low temperatures, respectively), and will be further shortened by triplet energy transfer to F8BT, consistent with the absence of triplet excited-state absorption from FIrpic.

To attribute the enhanced PIA signal in the blend film unambiguously to triplet energy transfer from FIrpic, we must rule out the possibility that FIrpic has an indirect effect by increasing the intersystem crossing in F8BT by inducing remote spin-orbit coupling.[25] This can be done by comparing the PIA spectrum excited in the UV (where the FIrpic is excited) with the corresponding spectrum excited at 501 nm (where only the F8BT is excited). As shown in Fig. 7, the PIA excited at 501 nm is much smaller than with excitation in the UV, despite the higher photon flux and higher optical density of the film at 501 nm. This confirms that the FIrpic does not significantly enhance intersystem crossing in the F8BT.

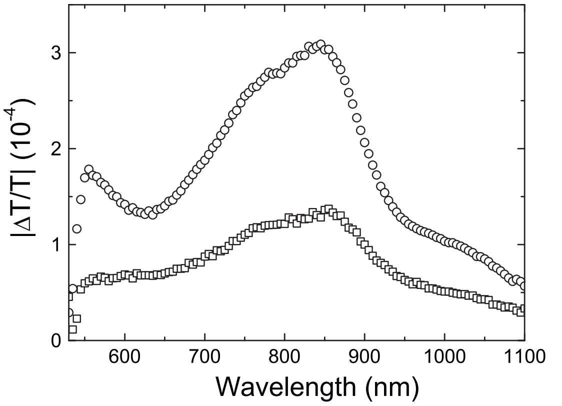

FIG. 7. PIA spectra of a FIrpic(5%)/F8BT blend film with excitation at 501 nm (squares) and by MLUV (circles). The laser intensity at 501 nm is 35 mW and that of the MLUV excitation is 24 mW.

Having established that efficient triplet energy transfer occurs from FIrpic to F8BT, we are now able to determine σ_T. First, we must establish the monomolecular lifetime τ.

Both monomolecular and bimolecular processes can be important in the decay of triplet excitons. For quantitative measurements, it is important to work in the low-intensity regime where monomolecular decay dominates. We have confirmed that the PIA signal increases linearly with excitation intensity up to the intensities of 50 mW cm^{-2} used in this work. Under these conditions, the lifetime of the absorbing state can be determined from the dependence of the PIA signal on modulation frequency. The in-phase lock-in signal should follow

$$\left|\frac{\Delta T}{T}\right|_X = \frac{G\sigma\tau}{1+\omega^2\tau^2}.$$

The triplet lifetimes calculated for pure F8BT and for the 5% blend film are shown in Table I. The slight increase in lifetime in the blend may be associated with morphological changes in the F8BT.

TABLE I. PIA of pristine F8BT and FIrpic(5%)/F8BT blend films at 40 K, excited by MLUV.

Blend (% FIrpic)	λ_{ex} (nm)	% absorption by FIrpic	PIA intensity at 845 nm	F8BT triplet measured lifetime (ms)
0%	MLUV	0%	1.0	0.38±0.01
5%	MLUV	3.0±0.2% (351 nm) 2.3±0.2% (364 nm)	3.1	0.42±0.01

The PIA obtained with F8BT and blend films at 40 K are summarized in Table I. The additional $\Delta T/T$ at 845 nm in the 5% blend is 2.1×10^{-4}, which we assume arises from triplets transferred from the FIrpic. The laser power incident on the sample is 24 mW, corresponding to $(3.6 \pm 0.1) \times 10^{16}$ photons/s absorbed within the probe beam area, taking into account reflection losses, the measured absorption spectrum, and the angle of incidence on the film. The molar absorbance of FIrpic was determined by measuring the optical density of a film of FIrpic dispersed in polymethyl methacrylate, where the FIrpic concentration and the film thickness were known. This was used to determine the fraction of the excitation in the PIA experiment absorbed by FIrpic in the 5% blend film. This fraction was found to be $(3.0 \pm 0.2)\%$ at 351 nm and $(2.3 \pm 0.2)\%$ at 364 nm, giving a total triplet generation rate of $(0.9 \pm 0.2) \times 10^{15}$ triplet excitons/s. The error arises from the determination of FIrpic molar absorbance, and from fluctuations between the two wavelength components (351 and 364 nm) present in the multiline ultraviolet (MLUV) laser source. Combining with the measured lifetime of 0.42 ± 0.01 ms gives a triplet population of $(3.9 \pm 0.8) \times 10^{11}$, corresponding to an average triplet density of $(6.9 \pm 1.5) \times 10^{11}$ cm^{-2} within the probe area. Combining with the measured $\Delta T/T$ gives a value of σ_T of 3.1×10^{-16} cm$^2 \pm 20\%$. This value compares well with the calculated value of $\sim 2 \times 10^{-16}$ cm^2,[14] which confirms the accuracy of the time-dependent density functional theory approach. We reemphasize that this value is considerably lower than for other conjugated polymers, which has been attributed to the weak electronic interactions between the monomer units in the F8BT. Our experimental value validates estimates of triplet densities in polymer blends that were based on the calculated value,[14] and also supports estimates of high singlet fractions in LEDs based on F8BT.[12]

IV. CONCLUSIONS

The triplet-triplet $(T_1 - T_n)$ excited-state absorption cross section of F8BT has been calculated from quasi-steady-state photoinduced absorption measurement films of F8BT blended with FIrpic. The enhanced induced absorption signal in the blend and the quenching of FIrpic emission provide evidence for efficient triplet energy transfer from FIrpic to the polymer. A value of 3.1×10^{-16} cm$^2 \pm 20\%$ at 845 nm is found for F8BT at 40 K, which agrees well with previous theoretical calculations.

ACKNOWLEDGMENTS

The work was supported by the Optoelectronics Collaboration of the Cavendish-KAIST Cooperation Program. The authors would like to thank Cambridge Display Technology Ltd. for the F8BT and Tae-Hyuk Kwon at Seoul National University, Korea, for synthesizing the FIrpic.

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