Organic Photovoltaics Using Tetraphenylbenzoporphyrin Complexes as Donor Layers

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As the demand for cost-competitive renewable energy options grows, considerable emphasis is being placed on new technologies for photovoltaic and photochemical energy conversion. One approach that shows promise involves the use of low-cost organic molecular and polymeric materials as the active layers in photovoltaic cells. The introduction of new materials that tune molecular electronic properties improving the photoconversion efficiency is important to advance in the practical application of organic solar cells.[1–3]

Typical organic photovoltaic cells (OPVs) are multilayer devices, consisting of electron donor (D) and acceptor (A) materials forming a heterojunction. Excitons created upon light absorption in either the D or A layer dissociate at the D/A interface, and the holes and electrons traverse the D and A materials, respectively, to be collected at the electrodes. Solar-to-electric energy conversion efficiency (η) is defined as the product of the short-circuit current density (J_{sc}), the open-circuit potential (V_{oc}), and the fill factor (*FF*), divided by the incident optical power ($\eta = J_{sc}\ V_{oc}\ FF/W_{opt}$), obtained under standard solar illumination conditions. The most efficient small-molecule-based planar heterojunction solar cell reported employs copper phthalocyanine (CuPc) as the donor layer and C_{60} as the acceptor.[1,4] To increase light conversion efficiency, it is important to identify new materials whose absorption yields improved overlap with the solar spectrum while maintaining both high carrier mobility and efficient exciton transport to the heterojunction.

Platinum tetraphenylbenzoporphyrin (PtTPBP) was recently found to be an efficient near-infrared electrophosphorescent material for use in organic light-emitting devices (OLEDs).[5] More relevant to OPVs is the extended electron conjugation of this molecule, relative to other Pt porphyrins, which results in higher optical extinction coefficients and a marked red-shift of the absorption in the visible region. PtTPBP is a nonplanar molecule with a saddle shape that may affect film morphology, and consequently, its electronic transport properties. In this paper we report the use of PtTPBP and the analogous structure with a Pd core as effective donor materials. Both Pt and Pd tetraphenylbenzoporphyrins are highly soluble in common organic solvents, making these compounds amenable to solution processing.

As shown previously,[5,6] the solution absorption spectra present an intense and sharp Soret band at wavelengths of $\lambda = 430$ nm and $\lambda = 444$ nm for PtTPBP and PdTPBP, respectively. The heavy central atoms and the ring structure affect the Q-band, resulting in a narrow and intense peak at $\lambda = 613$ nm (full width at half-maximum (FWHM) = 18 nm) for PtTPBP and $\lambda = 629$ nm for PdTPBP (FWHM = 22 nm). Film spectra of these compounds differ by only a minor red-shift and a slight broadening of the Soret and Q bands of both complexes compared to their solution spectra, as shown in Figure 1. X-ray diffraction studies of PtTPBP thin films indicate that they are amorphous. This is in contrast to reports for metal phthalocyanines[7] where extensive excitonic coupling due to aggregation significantly shifts the film spectra. For porphyrins, however, the absorption spectral dependence on film morphology is typically not as significant as in phthalocyanines.[8] Both PtTPBP and PdTPBP present an out-of-plane saddle shape arising from the repulsion of the bulky phenyl rings in the meso positions and the benzannulated pyrrole results in steric hindrance that reduces intermolecular interactions.[5]

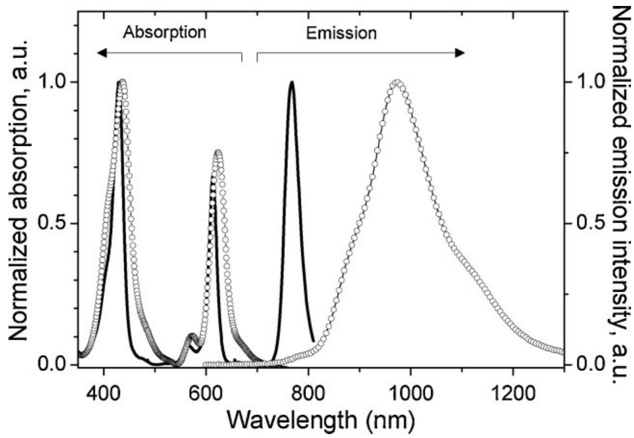

Figure 1. Absorption and emission spectra of PtTPBP in degassed toluene solution (solid line) and solid film (circles) at room temperature.

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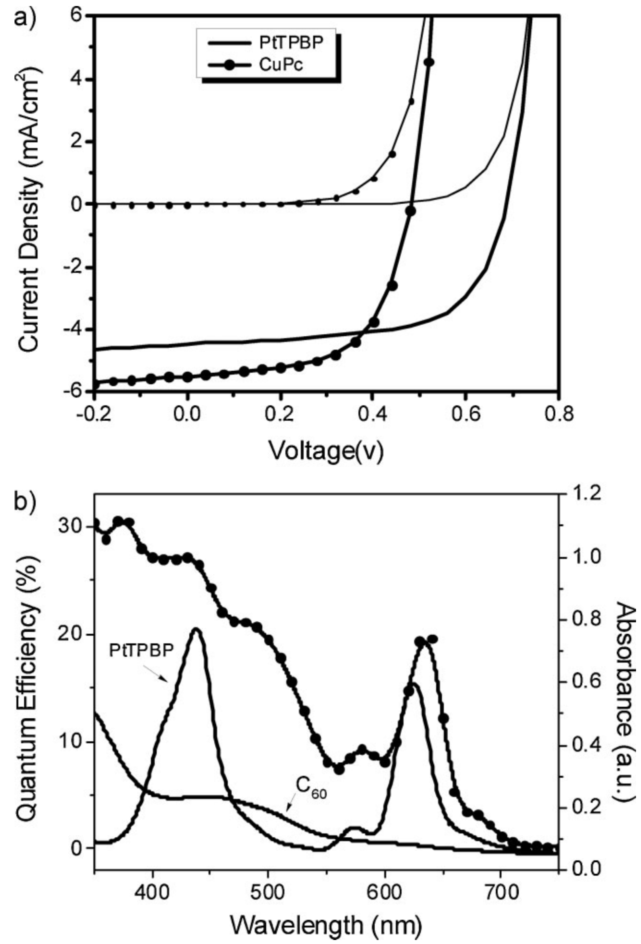

Figure 2. a) Current density versus voltage characteristics of ITO/CuPc(400 Å)/C_{60}(400 Å)/BCP(100 Å)/Al(1000 Å) (dotted line) and ITO/PtTPBP(150 Å)/C_{60}(400 Å)/BCP(100 Å)/Al(1000 Å) (solid line) under dark (thinner lines) and simulated AM1.5G illumination at 1sun intensity corrected to accurately match the solar spectrum. b) Quantum efficiency (dotted line) for the PtTPBP photovoltaic cell shown along with the absorption spectra of PtTPBP and C_{60}.

Figure 2a shows the current density versus voltage (J–V) characteristics for the cell structure: PtTPBP (150 Å)/C_{60} (400 Å)/BCP (100 Å)/Al (1000 Å), giving $J_{sc} = (4.48 \pm 0.05)$ mA cm^{-2}, $V_{oc} = (0.69 \pm 0.01)$ V, and $FF = (0.63 \pm 0.03)$ at 1 sun, AM1.5 G solar spectrally corrected power intensity. This corresponds to a power conversion efficiency of $\eta = (1.9 \pm 0.1)$ %, which is greater than a control CuPc/C_{60}/BCP/Al cell with $\eta = (1.6 \pm 0.1)$ % (see Table 1). The difference is primarily due to the higher V_{oc} of the Pt compound. A similar response is observed for devices employing PdTPBP, owing to its similar absorption spectrum and energy-level positions (see Table 1). The use of Ag instead of Al as the cathode material results in an increase of the J_{sc} by almost 10%, consistent with reports for CuPc devices with similar cathode compositions (see Supporting Information).[1,9] Previous reports using platinum octaethylporphine (PtOEP) as a donor material in OPVs suggested that in the absence of annealing, the series resistance is high, resulting in a low FF, and therefore a low efficiency.[3] In contrast, high fill factors are obtained using metal-TPBP donors, without the need for post-fabrication thermal treatment.

Table 1. Comparison of parameters for ITO/CuPc(400 Å)/C_{60}(400 Å)/BCP(100 Å)/Al(1000 Å) and ITO/metal-TPBP(150 Å)/C_{60}(400 Å)/BCP(100 Å)/Al(1000 Å) (M = Pt or Pd) under simulated AM1.5G light at 1 sun intensity corrected for mismatch to the solar spectrum.

	J_{sc} (mA cm^{-2}, $\pm$0.05)	V_{oc} (V, $\pm$0.01)	FF ($\pm$0.03)	η (%, $\pm$0.1)
CuPc	5.51	0.48	0.60	1.6
PtTPBP	4.48	0.69	0.63	1.9
PdTPBP	4.31	0.65	0.64	1.8

The J_{sc} for metal-TPBP devices is similar to those employing CuPc, which is remarkable considering the absorption bands for PtTPBP films are narrower than for CuPc, and the Soret band lies at the same wavelength as the principal C_{60} absorption band, resulting in a reduction in overlap with the AM1.5 spectrum. The external quantum efficiency for the PtTPBP device, along with the absorption spectra, is shown in Figure 2b. The observation of a high J_{sc} suggests that the reduced spectral coverage is compensated by an increased absorbance at $400 < \lambda < 700$ nm. This correlates with the high optical density (α) of the PtTPBP film which is more than double that of the CuPc film for the Q-band, where α_{CuPc} ($\lambda = 625$ nm) $= 8.06 \times 10^4$ cm^{-1}; α_{PtTPBP} ($\lambda = 625$ nm) $= 1.89 \times 10^5$ cm^{-1}; and α_{PdTPBP} ($\lambda = 635$ nm) $= 1.85 \times 10^5$ cm^{-1}.

To estimate the optimal metal-TPBP layer thickness, OPV cells with the structure ITO/metal-TPBP (xÅ)/C_{60} (400 Å)/BCP (100 Å)/Al (1000 Å) (BCP: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) were prepared, with results shown in Figure 3; a similar trend is observed for PdTPBP (Supporting Information). The series resistance (R_s) measured from dark J–V characteristics gradually increases as the PtTPBP layer thickness is increased (see Table 2). Here, FF depends only weakly on thickness, indicating that resulting variations in R_s do not significantly affect J_{sc}.

The thickness dependence is primarily due to the short exciton diffusion length which reduces the likelihood of excitons reaching the D/A interface prior to their decay. This conclusion

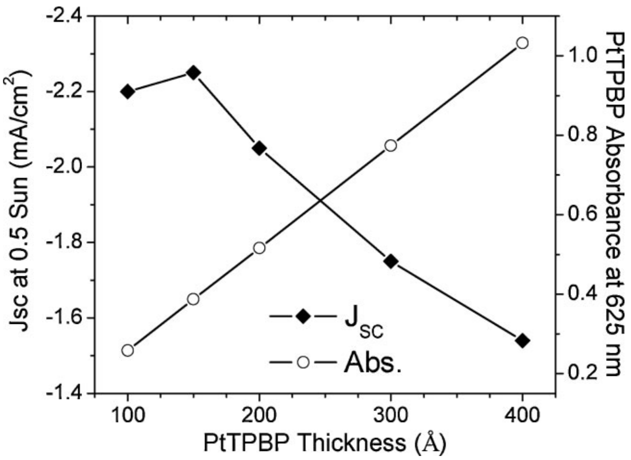

Figure 3. Current density versus layer thickness of ITO/PtTPBP(x = 100–400 Å)/C_{60}(400 Å)/BCP(100 Å)/Al(1000 Å) devices under simulated AM1.5G illumination at 50 mW cm^{-2}

Table 2. Photovoltaic performance parameters for devices ITO/PtTPBP(x Å)/C_{60}(400 Å)/BCP(100 Å)/Al(1000 Å) under simulated AM1.5G illumination at 50 mW cm^{-2}.

PtTPBP Thickness (Å)	J_{sc} (mA cm^{-2}, ±0.05)	V_{oc} (V, ±0.01)	FF (±0.01)	η (%, ±0.1)	R_s (Ω cm^2)
100	2.22	0.59	0.62	1.6	0.3
150	2.26	0.61	0.64	1.8	0.2
200	2.06	0.62	0.64	1.6	0.8
300	1.76	0.63	0.62	1.4	2.6
400	1.56	0.64	0.60	1.2	5.8

is supported by direct measurement of the diffusion length based on excited state quenching, resulting in $L_D = (57 \pm 5)$ Å for PtTPBP, as described in the Experimental section.

The origin of a short L_D for PtTPBP may be understood in terms of the excited state in the solid film. The emission spectrum of a PtTPBP film shows a broad, featureless band at $\lambda = 978$ nm that is significantly red-shifted relative to the solution (see Fig. 1) and the doped thin-film spectra of PtTPBP (solution and doped thin film PL spectra of PtTPBP are nearly identical).[5] Indeed, the thin-film absorption spectrum of PtTPBP shows only a minor bathochromic shift and broadening relative to the solution spectrum. These spectra suggest that they are due to excimers, or to a low concentration of dimer/aggregate states.[10,11] The excimer energy in PtTPBP is 0.34 eV, as inferred from the red-shift between the solution and thin-film emission spectra. This lower energy can act as an effective exciton trap, significantly influencing the exciton lifetime, and hence L_D.[11,12] Equally important may be trapping due to disorder-related defects arising from the sterically hindered molecular structure as discussed above.

An appealing attribute of metal-TPBP materials is their high solubility in common organic solvents. Hence, solution-processed devices were fabricated by spin-coating varying thicknesses of PtTPBP, followed by vacuum deposition of the C_{60} and BCP layers to achieve structures similar to the vacuum deposited devices discussed above. The $V_{oc} = (0.64 \pm 0.01)$ V and $FF = 0.52 \pm 0.03$ of solution-processed devices shown in Figure 4 are similar to those prepared by vacuum deposition, but give lower $J_{sc} = (2.47 \pm 0.05)$ mA cm^{-2} than the all-vacuum deposited devices (where $J_{sc} = (4.48 \pm 0.05)$ mA cm^{-2}, see Fig. 4). The variability in performance of solution-processed devices is considerably larger than when processed only in vacuum. For example, devices with a 150 Å thick layer of PtTPBP deposited from solution have V_{oc} ranging from 0.34V to 0.64 V, whereas the analogous devices with vacuum deposited PtTPBP vary only between 0.65V to 0.69V. The addition of a 50 Å layer of vapor-deposited PtTPBP between the solution processed PtTPBP film and C_{60} leads to devices with a narrow range of V_{oc} similar to those prepared entirely in vacuum.

In summary, we have demonstrated high efficiency, small-molecule organic solar cells using metal-TPBP as the donor layer. These molecules constitute an addition to the currently limited range of donor molecules that yield a 20% increase in efficiency when paired with the acceptor C_{60}. Devices showed a marked dependence of J_{sc} and efficiency on the porphyrin layer thickness. The optimal metal-TPBP thickness is 150 Å due to the short exciton diffusion length of 57 Å for these materials. Both vacuum and solution processing can be used for layer deposition with this family of donor materials.

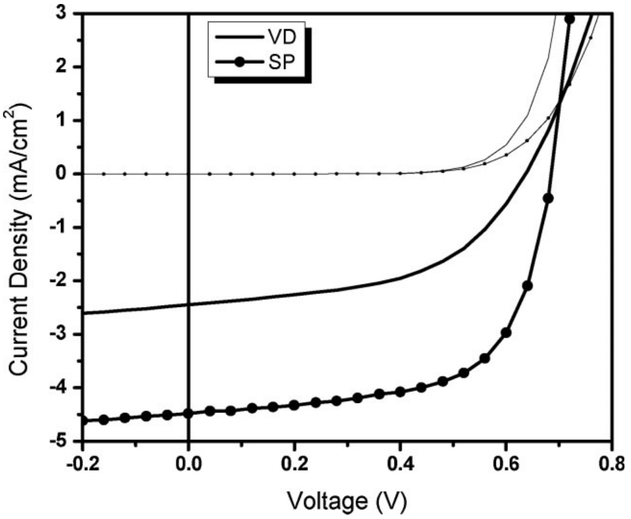

Figure 4. Comparison of devices with solution processed (SP) and vapor deposited (VD) donor layer. Dark and illuminated current density versus voltage characteristics corresponding to the following devices: PtTPBP(SP)(150 Å)/C_{60}(400 Å)/BCP(100 Å)/Al (filled circles); and PtTPBP (VD)(150 Å)/C_{60}(400 Å)/BCP(100 Å)/Al (solid line) under simulated 1 sun intensity, AM1.5G illumination.

Experimental

Photovoltaic cells were grown on solvent-cleaned 150 nm indium tin oxide (ITO)-coated glass ($R = (20 \pm 5)\ \Omega/\square$) substrates as described elsewhere [13], and subsequently exposed to UV-ozone for 10 min. immediately prior to loading into a high vacuum ($1–3 \times 10^{-6}$ Torr) chamber. Both Pt and Pd tetraphenylbenzoporphyrin were synthesized according to literature [5], and purified by vacuum thermal gradient sublimation. The organic materials, copper phthalocyanine (CuPc) 99% (Aldrich), fullerene (C_{60}) 99.5% (MTR Limited), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) 96% (Aldrich) were also purified by sublimation with one (C_{60}) or two (CuPc and BCP) cycles prior to use. Metal cathode materials, Al (99.999%) and Ag (99.9999%) (Alfa Aesar) were used as received. Materials were sequentially grown by vacuum thermal evaporation at the following rates: metal-TPBP (1 Å s^{-1}) or CuPc (2 Å s^{-1}), C_{60} (2 Å s^{-1}), and BCP (2 Å s^{-1}) and metals: 1000 Å thick Al (2 Å s^{-1}) or Ag (4 Å s^{-1}). The metal cathodes were evaporated through a shadow mask with 1 mm diameter openings. Current–voltage characteristics of the cells were measured in the dark and under simulated AM1.5G solar illumination (Oriel Instruments) using a Keithley 2420 3A Source Meter. Incident power was adjusted using a calibrated Si photodiode to match 1 sun intensity (100 mW cm^{-2}), and spectral response was measured using a Newport-Oriel monochromatic light source. Spectral mismatch was calculated and used to correct the measured efficiencies following standard procedures [14]. The data given in the text and tables are those for an average device and the error bars represent the variation in device performance among all of the devices tested on that substrate (typically 8–10 devices). Variability in device performance is greater when comparing devices on different substrates. We have seen the following ranges when we compared devices on five different substrates, with nominally the same structure (ITO/PtTPBP(150 Å)/C_{60}(400 Å)/BCP(100 Å)/Al, prepared by vacuum thermal evaporation): $\Delta J_{sc} = 0.5\ \mathrm{mA\,cm^{-2}}$; $\Delta V_{oc} = 0.02\ \mathrm{V}$; $\Delta FF = 0.05$ and $\Delta\eta = 0.5\%$. Absorption spectra were measured in a dichloromethane solution and for 300 Å thick films on quartz substrates using an Agilent ultraviolet/visible spectrometer. The exciton diffusion length was measured by spectrally resolved photoluminescence using C_{60} as the quenching layer and BCP as an exciton blocking layer [15].

For the solution-processed devices, thin films of the donor layer were spin-coated from 1 mL of a toluene solution of PtTPBP (5 mM), at 1500 rpm for 40 s to obtain a 150 Å thick layer onto previously cleaned ITO. The thickness was measured by ellipsometry and UV-vis absorption spectroscopy. The solution-deposited thin films were heated (90 °C) under vacuum for 10–20 min to remove any residual solvent. Once dried, the films were placed in the high vacuum chamber for deposition of C_{60}, BCP and Al layers following the procedures described above.

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[1] J. G. Xue, S. Uchida, B. P. Rand, S. R. Forrest, *Appl. Phys. Lett.* **2004**, *84*, 3013.

[2] a) K. L. Mutolo, E. I. Mayo, B. P. Rand, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* **2006**, *128*, 8108. b) B. P. Rand, J. Xue, F. Yang, S. R. Forrest, *Appl. Phys. Lett.* **2005**, *87*, 233508. c) R. F. Bailey-Salzman, B. P. Rand, S. R. Forrest, *Appl. Phys. Lett.* **2007**, *91*, 013508. d) S. Yoo, B. Domercq, B. Kippelen, *Appl. Phys. Lett.* **2004**, *85*, 5427. e) C. W. Chu, Y. Shao, V. Shrotriya, Y. Yang, *Appl. Phys. Lett.* **2005**, *86*, 243506.

[3] Y. Shao, Y. Yang, *Adv. Mater.* **2005**, *17*, 2841.

[4] P. Peumans, A. Yakimov, S. R. Forrest, *J. Appl. Phys.* **2003**, *93*, 3693.

[5] C. Borek, K. Hanson, P. I. Djurovich, M. E. Thompson, K. Aznavour, R. Bau, Y. Sun, S. R. Forrest, J. Brooks, L. Michalski, J. Brown, *Angew. Chem. Int. Ed.* **2007**, *46*, 1109.

[6] J. E. Rogers, K. A. Nguyen, D. C. Hufnagle, D. G. McLean, W. J. Su, K. M. Gossett, A. R. Burke, S. A. Vinogradov, R. Pachter, P. A. Fleitz, *J. Phys. Chem. A* **2003**, *107*, 11331.

[7] a) R. J. C. Brown, A. R. Kucernak, N. J. Long, C. Mongay-Batalla, *New J. Chem.* **2004**, *28*, 676. b) J. A. Ferreira, R. Barral, J. D. Baptista, M. I. C. Ferreira, *J. Lumin.* **1991**, *48–49*, 385.

[8] a) W. Stampor, *Chem. Phys.* **2004**, *305*, 77. b) L. K. Chau, C. D. England, S. Y. Chen, N. R. Armstrong, *J. Phys. Chem.* **1993**, *97*, 2699. c) J. Kalinowski, W. Stampor, J. Szmytkowski, M. Cocchi, D. Virgili, V. Fattori, P. D. Marco, *J. Chem. Phys.* **2005**, *122*, 154710. d) T. H. Tranthi, J. F. Lipskier, P. Maillard, M. Momenteau, J. M. Lopezcastillo, J. P. Jaygerin, *J. Phys. Chem.* **1992**, *96*, 1073. e) M. Gouterman, D. Holten, E. Lieberman, *Chem. Phys.* **1977**, *25*, 139.

[9] P. Peumans, S. R. Forrest, *Appl. Phys. Lett.* **2001**, *79*, 126.

[10] a) B. D'Andrade, S. R. Forrest, *Chem. Phys.* **2003**, *286*, 321. b) T. Dienel, H. Proehl, T. Fritz, K. Leo, *J. Lumin.* **2004**, *110*, 253. c) J. Kalinowski, W. Stampor, J. Szmytkowski, M. Cocchi, D. Virgili, V. Fattori, P. D. Marco, *J. Chem. Phys.* **2005**, *122*, 154710. d) S. W. Lai, M. C. W. Chan, T. C. Cheung, S. M. Peng, C. M. Che, *Inorg. Chem.* **1999**, *38*, 4046. e) B. W. Ma, P. I. Djurovich, S. Garon, B. Alleyne, M. E. Thompson, *Adv. Funct. Mater.* **2006**, *16*, 2438.

[11] B. Ma, P. I. Djurovich, M. E. Thompson, *Coord. Chem. Rev.* **2005**, *249*, 1501.

[12] a) W. L. Fleeman, W. B. Connick, *Comments Inorg. Chem.* **2002**, *23*, 205. b) K. T. Wan, C. M. Che, K. C. Cho, *J. Chem. Soc. Dalton Trans.* **1991**, 1077. c) N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, Mill Valley, CA **1991**.

[13] P. E. Burrows, Z. Shen, V. Bulovic, D. M. McCarty, S. R. Forrest, J. A. Cronin, M. E. Thompson, *J. Appl. Phys.* **1996**, *79*, 7991.

[14] V. Shrotriya, G. Li, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Adv. Funct. Mater.* **2006**, *16*, 2016.

[15] a) R. R. Lunt, N. C. Geibink, A. A. Belak, J. B. Benziger, S. R. Forrest, unpublished. b) G. Vaubel, H. Baessler, *Mol. Cryst. Liq. Cryst.* **1970**, *12*, 47.